

PHOTODEGRADATION-RESISTANT ELECTRODEPOSITABLE COATING  
COMPOSITIONS AND PROCESSES RELATED THERETO

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CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of priority from United States Provisional Applications 60/266,577 and 60/266,576, both filed February 5, 2001.

FIELD OF THE INVENTION

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The present invention is directed to an electrodepositable primer composition and a process for coating an electroconductive substrate using the composition. More particularly, the present invention is directed to multilayer composite coatings comprising a photodegradation-resistant electrodepositable primer composition and a top coat thereover, and to a process for forming such a composite coating on the substrate.

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BACKGROUND OF THE INVENTION

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Electrodeposition as a coating application method involves deposition of a film-forming composition onto a conductive substrate under the influence of an applied electrical potential. Electrodeposition has become increasingly important in the coatings industry because, by comparison with non-electrophoretic coating means, electrodeposition offers increased paint utilization, improved corrosion protection and low environmental contamination.

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Initially, electrodeposition was conducted with the workpiece to be coated serving as the anode. This was familiarly referred to as anionic electrodeposition. However, in 1972 cationic electrodeposition was introduced commercially and has continued to gain in popularity. Today, cationic electrodeposition is by far the prevalent method of electrodeposition. For example, a cationic primer coating is applied by electrodeposition to more that 80 percent of all motor vehicles produced throughout the world.

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Electrodepositable primer coating compositions, particularly those used in the automotive industry, typically are corrosion-resistant epoxy-based compositions crosslinked with aromatic isocyanates. If exposed to ultraviolet energy, such as sunlight, such compositions can undergo photodegradation. In some applications, a

FOOTNOTES

For example, if one or more top coats are sufficiently opaque to ultraviolet light transmission, such as by a high concentration of pigment and/or light absorbing compounds, little or no ultraviolet light can penetrate through the top coat(s) to the electrodeposited primer coating to cause photodegradation. However, if a thin top coat and/or a top coat which is not ultraviolet light absorbing is applied to the cured electrodeposited primer coating, ultraviolet light can pass through the top coat(s) resulting in photodegradation of the cured electrodeposited primer coating. Such a problem is likely to occur when a top coat is lightly pigmented with metal flake pigments which tend to allow transmission of visible and/or ultraviolet light to the previously applied and cured electrodeposited primer coating.

A variety of approaches are known to avoid photodegradation of the cured electrodeposited coatings. As mentioned above, top coats can be formulated to have a high concentration of pigments which provide ultraviolet light opacity. Further, top coat formulations can include additives to prevent or diminish the transmission of ultraviolet light such as ultraviolet light absorbers ("UVAS") and/or hindered amine light stabilizers ("HALS") which can be used in combination with anti-oxidants, for example, phenolic antioxidants.

Other factors can exacerbate the photosensitivity of an epoxy-based primer, thereby contributing to delamination of a subsequently applied top coat from the primer coating. Such factors include, but are not limited to, the use of aromatic isocyanate crosslinkers, and overbake of the electrodeposited primer coating at excessive times and/or temperatures..

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U.S. Patent No. 4,755,418 discloses a method of preventing the yellowing of the outermost coating of a multicoat coating system. The method comprises initially depositing onto a conductive substrate by cathodic electrodeposition a primer coating of at least one layer of an amine-epoxy resin adduct and a cross-linking agent; curing the primer to a hard, durable film; depositing a second coating onto the primer layer comprising at least one layer of a pigmented basecoat; depositing a third outermost coating onto the second coating comprising at least one layer of a clear top coat; and simultaneously curing the basecoat and the clear top coat. The electrodepositable primer coating composition contains a blocked polyisocyanate cross-linking agent selected from aliphatic polyisocyanates of at least six carbon atoms, the isocyanurates of aliphatic polyisocyanates, aromatic polyisocyanates having a molecular weight greater than 174, and the isocyanurates of aromatic diisocyanates having a molecular weight greater than 174.

U.S. Patent No. 5,205,916 discloses electrodepositable primer compositions containing an aqueous dispersion of an epoxy-based ionic resin and an antioxidant additive comprising a combination of a phenolic antioxidant and a sulfur-containing antioxidant. Such additives are disclosed as providing reduced overbake yellowing of the subsequently applied top coats as well as preventing intercoat delamination of these top coats upon exterior exposure.

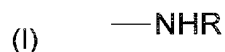
U.S. Patent No. 5,260,135 discloses photodegradation-resistant electrodepositable compositions comprising an epoxy-based ionic resin, a hindered amine light stabilizer present at levels of about 1 percent, and a phenolic antioxidant. Although effective for improving the resistance of the electrodeposited coating to photodegradation, the effect can vary somewhat due to the volatilization of the HALS present at the surface upon thermal curing of the composition. In some instances, the inclusion of HALS in electrodepositable coating compositions can provide only a marginal improvement for photodegradation resistance of the cured electrodeposited coating because the HALS can migrate into the subsequently applied top coating layers. Moreover, due to environmental and toxicity concerns, it is desirable to avoid the use of phenolic compounds such as the phenolic antioxidant mentioned above.

Although the aforementioned references disclose photodegradation resistant coating systems which can provide many advantages, each of the respective coating system disclosed therein can have one or more deficiencies, including excessive cost, toxicity issues, or marginal effectiveness. Accordingly, there remains a need in

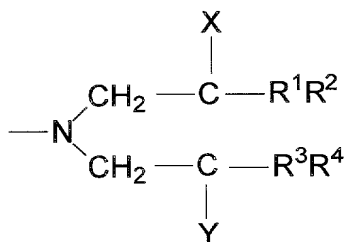
the coatings industry for a cost effective electrodepositable primer composition which retards photodegradation and delamination of subsequently applied top coats independent of the top coat composition(s).

## SUMMARY OF THE INVENTION

In one embodiment, the present invention is directed to an improved process for coating an electroconductive substrate. The process comprises (a) electrophoretically depositing on the substrate a curable electrodepositable coating composition to form an electrodeposited coating over at least a portion of the substrate; (b) heating the coated substrate to a temperature and for a time sufficient to cure the electrodeposited coating on the substrate; (c) applying directly to the cured electrodeposited coating one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions to form a top coat over at least a portion of the cured electrodeposited coating; (d) heating the coated substrate of step (c) to a temperature and for a time sufficient to cure the top coat, the cured top coat having at least 0.1 percent light transmission measured at 400 nanometers. The electrodepositable coating composition comprises a resinous phase dispersed in an aqueous medium, the resinous phase comprising: (1) one or more ungelled, active hydrogen-containing, cationic amine salt group-containing resins which are electrodepositable on a cathode, and (2) one or more at least partially blocked aliphatic polyisocyanate curing agents. The improvement comprises the presence in the curable electrodepositable coating composition of one or more cationic amine salt group-containing resins, wherein the amine salt groups are derived from pendant and/or terminal amine groups having the following structures (I) or (II):



or



(II)

wherein R represents H or C<sub>1</sub> to C<sub>18</sub> alkyl; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are the same or different, and each independently represents H or C<sub>1</sub> to C<sub>4</sub> alkyl; and X and Y can be the same or different, and each independently represents a hydroxyl group or an amino group..

The present invention is further directed to a process for forming a photodegradation-resistant multi-layer coating on an electroconductive substrate. The process comprises (a) electrophoretically depositing on the substrate a curable electrodepositable coating composition to form an electrodeposited coating over at least a portion of the substrate; (b) heating the coated substrate in an atmosphere having 5 parts per million or less of NO<sub>x</sub> to a temperature and for a time sufficient to cure the electrodeposited coating on the substrate; (c) applying directly to the cured electrodeposited coating one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions to form a top coat over at least a portion of the cured electrodeposited coating; and (d) heating the coated substrate of step (c) to a temperature and for a time sufficient to cure the top coat, the cured top coat having at least 0.1 percent light transmission measured at 400 nanometers. The electrodepositable coating composition comprises a resinous phase dispersed in an aqueous medium, the resinous phase comprising (1) one or more cationic polymers which are electrodepositable on a cathode, and (2) one or more at least partially blocked aliphatic polyisocyanate curing agents.

In another embodiment, the present invention provides a process for forming a photodegradation-resistant multi-layer coating on an electrically conductive substrate comprising (a) electrophoretically depositing on the substrate an aqueous, curable electrodepositable coating composition as described above to form an electrodeposited coating over at least a portion of the substrate, the substrate serving

as a cathode in an electrical circuit comprising the cathode and an anode, the cathode and the anode being immersed in the aqueous electrodepositable coating composition, wherein electric current is passed between the cathode and the anode to cause the coating to be electrodeposited over at least a portion of the substrate;

- 5 (b) heating the coated substrate at a temperature and for a time sufficient to cure the electrodeposited coating on the substrate; (c) applying directly to the cured electrodeposited coating one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions to form a top coat over at least a portion of the cured electrodeposited coating; and (d) heating the coated
- 10 substrate of step (c) to a temperature and for a time sufficient to cure the top coat, the cured top coat having at least 0.1 percent light transmission as measured at 400 nanometers. The improvement comprises the inclusion in the circuit of a non-ferrous anode.

- 15 In a further embodiment, the present invention is directed to an improved process for coating an electroconductive substrate comprising:  
(a) electrophoretically depositing on the substrate a curable electrodepositable coating composition to form an electrodeposited coating over at least a portion of the substrate; (b) heating the coated substrate to a temperature ranging from 250° to 400°F (121.1° to 204.4°C) for a time sufficient to cure the electrodeposited coating on
- 20 the substrate; (c) applying directly to the cured electrodeposited coating one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions to form a top coat over at least a portion of the cured electrodeposited coating; and (d) heating the coated substrate of step (c) to a temperature and for a time sufficient to cure the top coat, the cured top coat having 0.1 to 50 percent light
- 25 transmission as measured at 400 nanometers wavelength. The electrodepositable coating composition comprises a resinous phase dispersed in an aqueous medium, said resinous phase comprising (1) one or more active hydrogen-containing, cationic amine salt group-containing resins which are electrodepositable on a cathode, said resins selected from at least one of an acrylic polymer, a polyepoxide polymer, and mixtures thereof, and (2) one or more aliphatic polyisocyanate curing agents at least
- 30 partially blocked with one or more blocking agents selected from a 1,2-alkane diol having at least three carbon atoms, a benzylic alcohol, and mixtures thereof. The improvement comprises the presence in the curable electrodepositable composition of a resin having cationic amine salt groups which are derived from one or more

pendant and/or terminal amino groups having the structure (II) above, where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, X and Y are as described above for that structure. The process is characterized in that when the electrodepositable coating composition is electrodeposited and cured, at least two electron-withdrawing groups are bonded in the beta-position relative to substantially all of the amine nitrogen atoms.

The present invention is also directed to a photodegradation-resistant multi-layer composite coating comprising a cured primer coating layer over at least a portion of an electroconductive substrate, and a cured top coat layer over at least a portion of the cured primer coating layer. The primer coating layer is formed from a curable electrodepositable coating composition comprising a resinous phase dispersed in an aqueous medium, said resinous phase comprising (1) one or more active hydrogen-containing, cationic amine salt group-containing resins which are electrodepositable on a cathode, and (2) one or more at least partially blocked aliphatic polyisocyanate curing agents. The cationic salt groups of the resin (1) are derived from one or more pendant and/or terminal amino groups having the structure (I) or (II) above, where R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, X and Y are as described above for that structure. The top coat layer is formed from one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions. The multi-layer composite coating is characterized in that it exhibits substantially no interlayer delamination between the cured electrodeposited primer coating layer and the cured top coat layer upon concentrated solar spectral irradiance exposure equivalent to two years outdoor weathering when the top coat layer has at least 80 percent light transmission as measured at 400 nanometers.

In one embodiment, the present invention provides a photodegradation-resistant multi-layer composite coating comprising a cured primer coating layer over at least a portion of an electroconductive substrate, and a cured top coat layer over at least a portion of the cured primer layer. The primer coating layer is formed from a curable electrodepositable coating composition comprising a resinous phase dispersed in an aqueous medium, the resinous phase comprising (1) one or more active hydrogen-containing, cationic amine salt group-containing resins which are electrodepositable on a cathode, the resin being selected from an acrylic polymer, a polyepoxide polymer, and mixtures thereof; and (2) one or more aliphatic polyisocyanate curing agents at least partially blocked with a blocking agent selected from a 1,2-alkane diol having more than three carbon atoms, a benzylic alcohol, and

mixtures thereof. The resin (1) comprises cationic amine salt groups which are derived from one or more pendant and/or terminal amino groups having the structure (I) or (II) above, where R, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, X and Y are as described above for that structure. The top coat layer is formed from one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions. The multi-layer composite coating is characterized in that it exhibits substantially no interlayer delamination between the cured primer coating layer and the cured top coat layer upon concentrated solar spectral irradiance exposure equivalent to two years outdoor weathering when the top coat layer has at least 80 percent light transmission as measured at 400 nanometers.

In an alternative embodiment, the present invention is directed to a process for coating a metal substrate comprising the following steps:  
(a) electrophoretically depositing on the substrate a curable, electrodepositable coating composition; (b) heating the substrate to a temperature of 250°F to 400°F (121.1°C to 204.4°C) for a time sufficient to effect cure of the electrodepositable composition; (c) applying directly to the cured electrodepositable composition one or more pigment-containing coating compositions and/or one or more pigment-free top coating compositions to form a top coat thereover; and (d) heating the coated substrate to a temperature and for a time sufficient to effect cure of the one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions.

Also provided is a curable, electrodepositable coating composition used in the above alternative process, comprising (1) an active hydrogen-containing, cationic salt group-containing resin electrodepositable on a cathode, derived from a polyglycidyl ether of a polyhydric phenol that is essentially free of aliphatic carbon atoms to which are bonded more than one aromatic group; and (2) an at least partially blocked polyisocyanate curing agent essentially free of isocyanato groups or blocked isocyanato groups to which are bonded aromatic groups. This composition, when applied to a substrate and properly cured, then subjected to corrosion testing, such as a standard ASTM B117 salt spray test or a cyclic test such as GM Engineering Standard 9540P, Method B, will have no more scribe corrosion than exhibited by suitable controls containing aromatic isocyanates and/or Bisphenol A based aromatic polyepoxides. When top coated with a transparent base coat and /or clear coat composition having greater than 50% light transmission measured at 400



nanometers wave length, it will endure at least 1500 hours xenon arc accelerated weathering as per SAE J1960 without substantial degradation.

#### DETAILED DESCRIPTION OF THE INVENTION

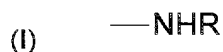
Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients, reaction conditions and so forth used in the specification and claims are to be understood as being modified in all instances by the term "about." Accordingly, unless indicated to the contrary, the numerical parameters set forth in the following specification and attached claims are approximations that may vary depending upon the desired properties sought to be obtained by the present invention. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claims, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

Notwithstanding that the numerical ranges and parameters setting forth the broad scope of the invention are approximations, the numerical values set forth in the specific examples are reported as precisely as possible. Any numerical values, however, inherently contain certain errors necessarily resulting from the standard deviation found in their respective testing measurements.

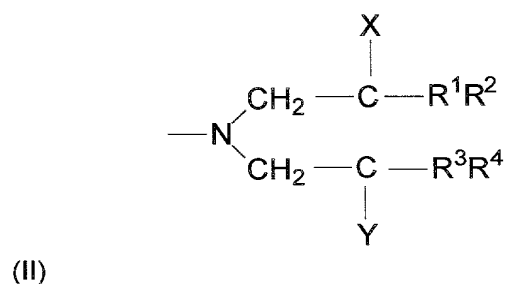
Also, it should be understood that any numerical range recited herein is intended to include all sub-ranges subsumed therein. For example, a range of 1" to 10" is intended to include all sub-ranges between and including the recited minimum value of 1 and the recited maximum value of 10, that is, having a minimum value equal to or greater than 1 and a maximum value of equal to or less than 10.

As mentioned above, in one embodiment, the present invention is directed to an improved process for coating an electroconductive substrate. The process comprises (a) electrophoretically depositing on the substrate a curable electrodepositable coating composition to form an electrodeposited coating over at least a portion of the substrate; (b) heating the coated substrate to a temperature and for a time sufficient to cure the electrodeposited coating on the substrate; (c) applying directly to the cured electrodeposited coating one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions to form a top coat over at least a portion of the cured electrodeposited coating; (d) heating the coated substrate of step (c) to a temperature and for a time sufficient to cure the top

coat, the cured top coat having at least 0.1 percent light transmission measured at 400 nanometers. The electrodepositable coating composition comprises a resinous phase dispersed in an aqueous medium, the resinous phase comprising: (1) one or more ungelled, active hydrogen-containing, cationic amine salt group-containing  
 5 resins which are electrodepositable on a cathode, and (2) one or more at least partially blocked aliphatic polyisocyanate curing agents. The amine salt groups of the cationic resin (1) are derived from pendant and/or terminal amine groups having the following structures (I) or (II):



or



15 wherein R represents H or C<sub>1</sub> to C<sub>18</sub> alkyl; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are the same or different, and each independently represents H or C<sub>1</sub> to C<sub>4</sub> alkyl; and X and Y can be the same or different, and each independently represents a hydroxyl group or an amino group.

In the processes of the present invention, the curable electrodepositable  
 20 coating composition can be electrophoretically deposited onto at least a portion of any of a variety of electroconductive substrates, including various metallic substrates. Suitable metallic substrates can include ferrous metals and non-ferrous metals. Suitable ferrous metals include iron, steel, and alloys thereof. Non-limiting examples of useful steel materials include cold-rolled steel, galvanized (i.e., zinc coated) steel,  
 25 electrogalvanized steel, stainless steel, pickled steel, GALVANNEAL®, GALVALUME®, AND GALVAN® zinc-aluminum alloys coated upon steel, and combinations thereof. Useful non-ferrous metals include conductive carbon coated materials, aluminum, copper, zinc, magnesium and alloys thereof. Cold rolled steel

also is suitable when pretreated with a solution such as a metal phosphate solution, an aqueous solution containing at least one Group IIIB or IVB metal, an organophosphate solution, an organophosphonate solution and combinations of the above as are discussed below. Combinations or composites of ferrous and non-ferrous metals can also be used.

The electrodepositable coating compositions of the present invention can be applied to either bare metal or pretreated metal substrates. By "bare metal" is meant a virgin metal substrate that has not been treated with a pretreatment composition such as conventional phosphating solutions, heavy metal rinses and the like. Additionally, for purposes of the present invention, 'bare metal' substrates can include a cut edge of a substrate that is otherwise treated and/or coated over the non-edge surfaces of the substrate.

Before any treatment or application of any coating composition, the substrate optionally may be formed into an object of manufacture. A combination of more than one metal substrate can be assembled together to form such an object of manufacture.

Also, it should be understood that as used herein, an electrodepositable composition or coating formed "over" at least a portion of a "substrate" refers to a composition formed directly on at least a portion of the substrate surface, as well as a composition or coating formed over any coating or pretreatment material which was previously applied to at least a portion of the substrate.

That is, the "substrate" upon which the coating composition is electrodeposited can comprise any electroconductive substrates including those described above to which one or more pretreatment and/or primer coatings have been previously applied. For example, the "substrate" can comprise a metallic substrate and a weldable primer coating over at least a portion of the substrate surface. The electrodepositable coating composition described above is then electrodeposited and cured over at least a portion thereof. One or more top coating compositions as described in detail below are subsequently applied over at least a portion of the cured electrodeposited coating.

For example, the substrate can comprise any of the foregoing electroconductive substrates and a pre-treatment composition applied over at least a portion of the substrate, the pretreatment composition comprising a solution that contains one or more Group IIIB or IVB element-containing compounds, or mixtures

thereof, solubilized or dispersed in a carrier medium, typically an aqueous medium. The Group IIIB and IVB elements are defined by the CAS Periodic Table of the Elements as shown, for example, in the Handbook of Chemistry and Physics, (60th Ed. 1980). Transition metal compounds and rare earth metal compounds typically  
5 are compounds of zirconium, titanium, hafnium, yttrium and cerium and mixtures thereof. Typical zirconium compounds may be selected from hexafluorozirconic acid, alkali metal and ammonium salts thereof, ammonium zirconium carbonate, zirconyl nitrate, zirconium carboxylates and zirconium hydroxy carboxylates such as hydrofluorozirconic acid, zirconium acetate, zirconium oxalate, ammonium zirconium  
10 glycolate, ammonium zirconium lactate, ammonium zirconium citrate, and mixtures thereof.

The pretreatment composition carrier also can contain a film-forming resin, for example, the reaction products of one or more alkanolamines and an epoxy-  
15 functional material containing at least two epoxy groups, such as those disclosed in U.S. 5,653,823. Other suitable resins include water soluble and water dispersible polyacrylic acids such as those as disclosed in U. S. Patent Nos. 3,912,548 and 5,328,525; phenol-formaldehyde resins as described in U. S. Patent 5,662,746, incorporated herein by reference; water soluble polyamides such as those disclosed in WO 95/33869; copolymers of maleic or acrylic acid with allyl ether as described in  
20 Canadian patent application 2,087,352; and water soluble and dispersible resins including epoxy resins, aminoplasts, phenol-formaldehyde resins, tannins, and polyvinyl phenols as discussed in U. S. Patent 5,449,415.

Further, non-ferrous or ferrous substrates can be pretreated with a non-insulating layer of organophosphates or organophosphonates such as those  
25 described in U.S. Patents No 5,294,265 and 5,306,526. Such organophosphate or organophosphonate pretreatments are available commercially from PPG Industries, Inc. under the trade name NUPAL®. Application to the substrate of a non-conductive coating, such as NUPAL, typically is followed by the step of rinsing the substrate with deionized water prior to the coalescing of the coating. This ensures that the layer of  
30 the non-conductive coating is sufficiently thin to be non-insulating, i.e., sufficiently thin such that the non-conductive coating does not interfere with electroconductivity of the substrate, allowing subsequent electrodeposition of a electrodepositable coating composition. The pretreatment coating composition can further comprise surfactants that function as aids to improve wetting of the substrate. Generally, the

surfactant materials are present in an amount of less than about 2 weight percent on a basis of total weight of the pretreatment coating composition. Other optional materials in the carrier medium include defoamers and substrate wetting agents.

Due to environmental concerns, the pretreatment coating composition can be free of chromium-containing materials, i.e., the composition contains less than about 2 weight percent of chromium-containing materials (expressed as  $\text{CrO}_3$ ), typically less than about 0.05 weight percent of chromium-containing materials.

In a typical pre-treatment process, before depositing the pre-treatment composition upon the surface of the metal substrate, it is usual practice to remove foreign matter from the metal surface by thoroughly cleaning and degreasing the surface. The surface of the metal substrate can be cleaned by physical or chemical means, such as by mechanically abrading the surface or cleaning/degreasing with commercially available alkaline or acidic cleaning agents which are well known to those skilled in the art, such as sodium metasilicate and sodium hydroxide. A non-limiting example of a suitable cleaning agent is CHEMKLEEN® 163, an alkaline-based cleaner commercially available from PPG Pretreatment and Specialty Products of Troy, Michigan. Acidic cleaners also can be used. Following the cleaning step, the metal substrate is usually rinsed with water in order to remove any residue. The metal substrate can be air-dried using an air knife, by flashing off the water by brief exposure of the substrate to a high temperature or by passing the substrate between squeegee rolls. The pretreatment coating composition can be deposited upon at least a portion of the outer surface of the metal substrate. Preferably, the entire outer surface of the metal substrate is treated with the pretreatment composition. The thickness of the pretreatment film can vary, but is generally less than about 1 micrometer, preferably ranges from about 1 to about 500 nanometers, and more preferably ranges from about 10 to about 300 nanometers.

The pretreatment coating composition is applied to the surface of the metal substrate by any conventional application technique, such as by spraying, immersion or roll coating in a batch or continuous process. The temperature of the pretreatment coating composition at application is typically about 10°C to about 85°C, and preferably about 15°C to about 60°C. The pH of the pretreatment coating composition at application generally ranges from 2.0 to 5.5, and typically from 3.5 to 5.5. The pH of the medium may be adjusted using mineral acids such as hydrofluoric acid, fluoroboric acid, phosphoric acid, and the like, including mixtures thereof;

organic acids such as lactic acid, acetic acid, citric acid, sulfamic acid, or mixtures thereof; and water soluble or water dispersible bases such as sodium hydroxide, ammonium hydroxide, ammonia, or amines such as triethylamine, methylethyl amine, or mixtures thereof.

Continuous processes typically are used in the coil coating industry and also for mill application. The pretreatment coating composition can be applied by any of these conventional processes. For example, in the coil industry, the substrate typically is cleaned and rinsed and then contacted with the pretreatment coating composition by roll coating with a chemical coater. The treated strip is then dried by heating, painted and baked by conventional coil coating processes.

Mill application of the pretreatment composition can be by immersion, spray or roll coating applied to the freshly manufactured metal strip. Excess pretreatment composition is typically removed by wringer rolls. After the pretreatment composition has been applied to the metal surface, the metal can be rinsed with deionized water and dried at room temperature or at elevated temperatures to remove excess moisture from the treated substrate surface and cure any curable coating components to form the pretreatment coating. Alternatively, the treated substrate can be heated to a temperature ranging from 65°C to 125°C for 2 to 30 seconds to produce a coated substrate having a dried residue of the pretreatment coating composition thereon. If the substrate is already heated from the hot melt production process, no post application heating of the treated substrate is required to facilitate drying. The temperature and time for drying the coating will depend upon such variables as the percentage of solids in the coating, components of the coating composition and type of substrate.

The film coverage of the residue of the pretreatment composition generally ranges from 1 to 10,000 milligrams per square meter (mg/m<sup>2</sup>), and usually from 10 to 400 mg/m<sup>2</sup>.

A layer of a weldable primer also can be applied to the substrate, whether or not the substrate has been pretreated. A typical weldable primer is BONA-ZINC®, a zinc-rich mill applied organic film-forming composition, which is commercially available from PPG Industries, Inc., Pittsburgh, Pennsylvania. BONA-ZINC can be applied to a thickness of at least 1 micrometer and typically to a thickness of 3 to 4 micrometers. Other weldable primers, such as iron phosphide-rich primers, are commercially available.

The electrodeposition process of the present invention typically involves immersing the electroconductive substrate into an electrodeposition bath of an aqueous electrodepositable composition, the substrate serving as a cathode in an electrical circuit comprising the cathode and an anode. Sufficient electrical current is applied between the electrodes to deposit a substantially continuous, adherent film of the electrodepositable coating composition onto at least a portion of the surface of the electroconductive substrate. Electrodeposition is usually carried out at a constant voltage in the range of from 1 volt to several thousand volts, typically between 50 and 500 volts. Current density is usually between 1.0 ampere and 15 amperes per square foot (10.8 to 161.5 amperes per square meter) and tends to decrease quickly during the electrodeposition process, indicating formation of a continuous, self-insulating film.

Any of a variety of electrodepositable coating compositions can be used in the processes of the present invention. In a particular embodiment of the present invention, the electrodepositable coating composition comprises a resinous phase dispersed in an aqueous medium, the resinous phase comprising (1) one or more ungelled, cationic resins or polymers, typically an active hydrogen group-containing, cationic amine salt group-containing polymer, which are electrodepositable on a cathode; and (2) one or more at least partially blocked aliphatic polyisocyanate curing agents.

Cationic polymers suitable for use in the electrodepositable coating compositions, typically as the main film-forming polymer, can include any of a number of cationic polymers well known in the art so long as the polymers are "water dispersible," i.e., adapted to be solubilized, dispersed or emulsified in water. Such polymers comprise cationic functional groups to impart a positive charge.

By "ungelled" is meant the resins are substantially free of crosslinking and have an intrinsic viscosity when dissolved in a suitable solvent, as determined, for example, in accordance with ASTM-D1795 or ASTM-D4243. The intrinsic viscosity of the reaction product is an indication of its molecular weight. A gelled reaction product, on the other hand, since it is of essentially infinitely high molecular weight, will have an intrinsic viscosity too high to measure. As used herein, a reaction product that is "substantially free of crosslinking" refers to a reaction product that has a weight average molecular weight (Mw), as determined by gel permeation chromatography, of less than 1,000,000.

Also, as used herein, the term "polymer" is meant to refer to oligomers and both homopolymers and copolymers. Unless stated otherwise, as used in the specification and the claims, molecular weights are number average molecular weights for polymeric materials indicated as "Mn" and obtained by gel permeation chromatography using polystyrene standards in an art-recognized manner.

Suitable examples of such cationic film-forming resins can include active hydrogen-containing, cationic polymers selected from one or more of a polyepoxide polymer, an acrylic polymer, a polyurethane polymer, a polyester polymer, mixtures thereof, and copolymers thereof, for example a polyester-polyurethane polymer.

Typically, the resin (1) comprises a polyepoxide polymer, or a mixture of a polyepoxide polymer and an acrylic polymer. As aforementioned, the polymers which are suitable for use as the cationic resin (1), comprise active hydrogens as curing reaction sites. The term "active hydrogen" refers to those groups which are reactive with isocyanates as determined by the Zerewitnoff test as is described in the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, Vol. 49, page 3181 (1927). In one embodiment of the present invention, the active hydrogens are derived from hydroxyl groups, primary amine groups and/or secondary amine groups.

Any of a variety of polyepoxides known in the related art can be used to form the cationic resin (1). Examples of polyepoxides which are suitable for this purpose include those having a 1,2-epoxy equivalency greater than one, and typically two; that is, polyepoxides that have on average two epoxide groups per molecule. Such polyepoxide polymers can include the polyglycidyl ethers of cyclic polyols, for example polyhydric phenols, such as Bisphenol A. These polyepoxides can be prepared by etherification of polyhydric phenols with an epihalohydrin or dihalohydrin such as epichlorohydrin or dichlorohydrin in the presence of alkali. Nonlimiting examples of suitable polyhydric phenols include 2,2-bis-(4-hydroxyphenyl)propane, 1,1-bis-(4-hydroxyphenyl)ethane, 2-methyl-1,1-bis-(4-hydroxyphenyl)propane, 2,2-(4-hydroxy-3-tertiarybutylphenyl)propane, and bis-(2-hydroxynaphthyl)methane

Besides polyhydric phenols, other cyclic polyols can be used to prepare the polyglycidyl ethers of cyclic polyol derivatives. Examples of such cyclic polyols include alicyclic polyols, such as cycloaliphatic polyols, for example 1,2-cyclohexanediol, 1,4-cyclohexanediol, 1,2-bis-(hydroxymethyl)cyclohexane, 1,3-bis-(hydroxymethyl)cyclohexane and hydrogenated bisphenol A.



The polyepoxides can be chain-extended with a polyether or a polyester polyol. Examples of suitable polyether polyols and conditions for chain extension are disclosed in U.S. Patent No. 4,468,307. Examples of polyester polyols for chain extension are disclosed in U.S. Patent No. 4,148,772.

5 Other suitable polyepoxides can be produced similarly from novolak resins or similar polyphenols. Such polyepoxide resins are described in U.S. Patent Nos. 3,663,389; 3,984,299; 3,947,338; and 3,947,339. Additional polyepoxide resins which are suitable for use in forming the cationic resin (1) include those described in U.S. Patent Nos. 4,755,418, 5,948,229 and 6,017,432.

10 Suitable acrylic polymers from which the active hydrogen-containing, cationic salt group-containing polymer may be derived can include copolymers of one or more alkyl esters of acrylic acid or methacrylic acid, optionally together with one or more other polymerizable ethylenically unsaturated monomers. Suitable alkyl esters of acrylic acid or methacrylic acid include methyl methacrylate, ethyl methacrylate, butyl methacrylate, ethyl acrylate, butyl acrylate, and 2-ethyl hexyl acrylate. Suitable other copolymerizable ethylenically unsaturated monomers include nitriles such acrylonitrile and methacrylonitrile, vinyl and vinylidene halides such as vinyl chloride and vinylidene fluoride and vinyl esters such as vinyl acetate. Acid and anhydride functional ethylenically unsaturated monomers such as acrylic acid, methacrylic acid or anhydride, itaconic acid, maleic acid or anhydride, or fumaric acid may be used. Amide functional monomers including, acrylamide, methacrylamide, and N-alkyl substituted (meth)acrylamides are also suitable. Vinyl aromatic compounds such as styrene and vinyl toluene can be used so long as photodegradation resistance of the polymer and the resulting electrodeposited coating is not compromised.

25 Functional groups such as hydroxyl and amino groups can be incorporated into the acrylic polymer by using functional monomers such as hydroxyalkyl acrylates and methacrylates or aminoalkyl acrylates and methacrylates. Epoxide functional groups (for conversion to cationic salt groups) may be incorporated into the acrylic polymer by using functional monomers such as glycidyl acrylate and methacrylate, 3,4-epoxycyclohexylmethyl(meth)acrylate, 2-(3,4-epoxycyclohexyl)ethyl(meth)acrylate, or allyl glycidyl ether. Alternatively, epoxide functional groups may be incorporated into the acrylic polymer by reacting carboxyl groups on the acrylic polymer with an epihalohydrin or dihalohydrin such as epichlorohydrin or dichlorohydrin. The acrylic polymer can be prepared by traditional

free radical initiated polymerization techniques, such as solution or emulsion polymerization, as known in the art using suitable catalysts which include organic peroxides and azo type compounds and optionally chain transfer agents such as alpha-methyl styrene dimer and tertiary dodecyl mercaptan. Additional acrylic polymers which are suitable for forming the active hydrogen-containing, cationic amine salt group-containing resin (1) which is used in the electrodepositable compositions of the present invention include, those resins described in U.S. Patent Nos. 3,455,806 and 3,928,157.

Besides the above-described polyepoxide and acrylic polymers, the active hydrogen-containing, cationic salt group-containing polymer can be derived from a polyester. Such polyesters can be prepared in a known manner by condensation of polyhydric alcohols and polycarboxylic acids. Suitable polyhydric alcohols include, for example, ethylene glycol, propylene glycol, butylene glycol, 1,6-hexylene glycol, neopentyl glycol, diethylene glycol, glycerol, trimethylol propane, and pentaerythritol. Examples of suitable polycarboxylic acids used to prepare the polyester include succinic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, phthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, and trimellitic acid. Besides the polycarboxylic acids mentioned above, functional equivalents of the acids such as anhydrides where they exist or lower alkyl esters of the acids such as the methyl esters may be used.

The polyesters contain a portion of free hydroxyl groups (resulting from the use of excess polyhydric alcohol and/or higher polyols during preparation of the polyester) which are available for cure reactions. Epoxide functional groups may be incorporated into the polyester by reacting carboxyl groups on the polyester with an epihalohydrin or dihalohydrin such as epichlorohydrin or dichlorohydrin..

Amino groups can be incorporated into the polyester polymer by reacting epoxy functional groups of the polymer with a hydroxyl containing tertiary amine, for example, N,N-dialkylalkanolamines and N-alkyldialkanolamines. Specific examples of suitable tertiary amines include those N-alkyl dialkanolamines disclosed in U. S. Patent No. 5,483,012, at column 3, lines 49-63. Suitable polyesters for use in the process of the present invention include those disclosed in U. S. Patent No. 3,928,157.

Polyurethanes can also be used as the polymer from which the active hydrogen-containing, cationic salt group-containing resin can be derived. Among the

polyurethanes which can be used are polymeric polyols which are prepared by reacting polyester polyols or acrylic polyols such as those mentioned above with a polyisocyanate such that the OH/NCO equivalent ratio is greater than 1:1 so that free hydroxyl groups are present in the product. Smaller polyhydric alcohols such as  
 5 those disclosed above for use in the preparation of the polyester may also be used in place of or in combination with the polymeric polyols.

Additional examples of polyurethane polymers suitable for forming the active hydrogen-containing, cationic amine salt group-containing resin (1) include the polyurethane, polyurea, and poly(urethane-urea) polymers prepared by reacting  
 10 polyether polyols and/or polyether polyamines with polyisocyanates. Such polyurethane polymers are described in U.S. Patent No. 6,248,225.

Hydroxyl functional tertiary amines such as N,N-dialkylalkanolamines and N-alkyl dialkanolamines may be used in combination with the other polyols in the preparation of the polyurethane. Examples of suitable tertiary amines include those  
 15 N-alkyl dialkanolamines disclosed in U. S. Patent No. 5,483,012, at column 3, lines 49-63.

Epoxide functional groups may be incorporated into the polyurethane by methods well known in the art. For example, epoxide groups can be incorporated by reacting hydroxyl groups on the polyurethane with an epihalohydrin or dihalohydrin  
 20 such as epichlorohydrin or dichlorohydrin in the presence of alkali.

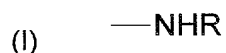
Mixtures of the polymers described above also can advantageously be used. In one embodiment of the present invention the cationic resin (1) comprises a mixture of a cationic polyepoxide polymer and a cationic acrylic polymer. Where such mixtures are used, the polyepoxide polymer can be present in the  
 25 electrodepositable coating compositions in an amount ranging from 10 to 90, typically 20 to 80 weight percent, based on total weight of resin solids present in the composition.

The polymers used in the electrodepositable coating composition of the present invention can have number average molecular weights (Mn) ranging from  
 30 1000 to 20,000, often from 1000 to 8000, and typically from 1000 to 5000, depending on the type of resin used, as determined by gel permeation chromatography using a polystyrene standard.

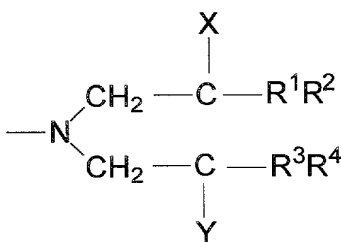
The active hydrogen-containing resin (1) comprises cationic amine salt groups which are derived from pendant and/or terminal amino groups. By "terminal

and/or pendant" is meant that primary and/or secondary amino groups are present as a substituent which is pendant from or in the terminal position of the polymeric backbone, or, alternatively, is an end-group substituent of a group which is pendant and/or terminal from the polymer backbone. In other words, the amino groups from which the cationic amine salt groups are derived are not within the polymeric backbone.

The pendant and/or terminal amino groups can have the following structures (I) or (II):



or



(II)

wherein R represents H or C<sub>1</sub> to C<sub>18</sub> alkyl; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are the same or different, and each independently represents H or C<sub>1</sub> to C<sub>4</sub> alkyl; and X and Y can be the same or different, and each independently represents a hydroxyl group or an amino group.

By "alkyl" is meant alkyl and aralkyl, cyclic or acyclic, linear or branched monovalent hydrocarbon groups. The alkyl groups can be unsubstituted or substituted with one or more heteroatoms, for example, non-carbon, non-hydrogen atoms such as one or more oxygen, nitrogen or sulfur atoms.

The pendant and/or terminal amino groups represented by structures (I) and (II) above can be derived from a compound selected from the group consisting of ammonia, methylamine, diethanolamine, diisopropanolamine, N-hydroxyethyl ethylenediamine, diethylenetriamine, and mixtures thereof. One or more of these compounds is reacted with one or more of the above described polymers, for example, a polyepoxide polymer, where the epoxy groups are ring-opened via

reaction with a polyamine, thereby providing terminal amino groups and secondary hydroxyl groups.

In one particular embodiment of the invention, the cationic salt group-containing polymer contains amine salt groups which are derived from one or more pendant and/or terminal amino groups having the structure (II) above, such that when the electrodepositable coating composition is electrodeposited and cured, at least two electron-withdrawing groups (as described in detail below) are bonded in the beta-position relative to substantially all of the nitrogen atoms present in the cured electrodeposited coating. In a further embodiment of the invention, when the electrodepositable coating composition is electrodeposited and cured, three electron-withdrawing groups are bonded in the beta-position relative to substantially all of the nitrogen atoms present in the cured electrodeposited coating. By "substantially all" of the nitrogen atoms present in the cured electrodeposited coating is meant at least 65 percent, and typically 90 percent, of all nitrogen atoms present in the cured electrodeposited coating which are derived from the amine used to form the cationic amine salt groups.

As discussed below, the electron-withdrawing groups to which reference is made herein are formed by the reaction of the polyisocyanate curing agent (2) with the pendant and/or terminal hydroxyl and/or amino groups represented by X and Y in structure (II) which are bonded in the beta-position relative to the nitrogen atom depicted in this structure. The amount of free or unbound amine nitrogen present in a cured free film of the electrodepositable composition can be determined as follows. The cured free coating film can be cryogenically milled and dissolved with acetic acid then titrated potentiometrically with acetous perchloric acid to determine the total base content of the sample. The primary amine content of the sample can be determined by reaction of the primary amine with salicylaldehyde to form an untitratable azomethine. Any unreacted secondary and tertiary amine then can be determined by potentiometric titration with perchloric acid. The difference between the total basicity and this titration represents the primary amine. The tertiary amine content of the sample can be determined by potentiometric titration with perchloric acid after reaction of the primary and secondary amine with acetic anhydride to form the corresponding amides.

In one embodiment of the present invention, the terminal amino groups have the structure (II) where both X and Y comprise primary amino groups, e.g., the amino

group is derived from diethylenetriamine. It should be understood that in this instance, prior to reaction with the polymer, the primary amino groups can be blocked, for example, by reaction with a ketone such as methyl ethyl ketone, to form the diketimine. Such ketimines are those described in U. S. Patent No. 4,104,147, column 6, line 23 to column 7, line 23. The ketimine groups can decompose upon dispersing the amine-epoxy reaction product in water, thereby providing free primary amine groups as curing reaction sites.

Minor amounts (e.g., an amount which would represent less than or equal to 5 percent of total amine nitrogen present in the composition) of amines such as mono, di, and trialkylamines and mixed aryl-alkyl amines which do not contain hydroxyl groups, or amines substituted with groups other than hydroxyl provided that the inclusion of such amines does not negatively affect the photodegradation resistance of the cured electrodeposited coating. Specific examples include monoethanolamine, N-methylethanolamine, ethylamine, methylethylamine, triethylamine, N-benzyl dimethylamine, dicocoamine and N,N-dimethylcyclohexylamine.

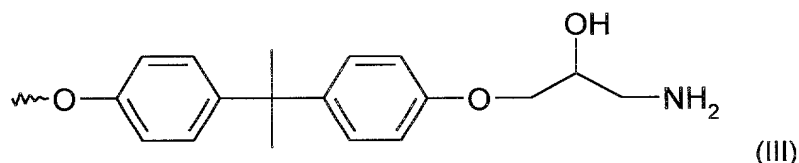
The reaction of the above-described amines with epoxide groups on the polymer takes place upon mixing of the amine and polymer. The amine may be added to the polymer or vice versa. The reaction can be conducted neat or in the presence of a suitable solvent such as methyl isobutyl ketone, xylene, or 1-methoxy-2-propanol. The reaction is generally exothermic and cooling may be desired. However, heating to a moderate temperature of about 50°C to 150°C may be done to hasten the reaction.

The active hydrogen-containing, cationic salt group-containing polymer used in the electrodeposable composition is prepared from components selected so as to maximize the photodegradation resistance of the polymer and the resulting cure electrodeposited composition. Though not intending to be bound by any theory, it is believed that photodegradation resistance ( i.e., resistance to visible and ultraviolet degradation) of the cured electrodeposited coating can be correlated with the location and nature of nitrogen-containing cationic groups used for dispersion of the active hydrogen-containing, cationic amine salt group-containing resin.

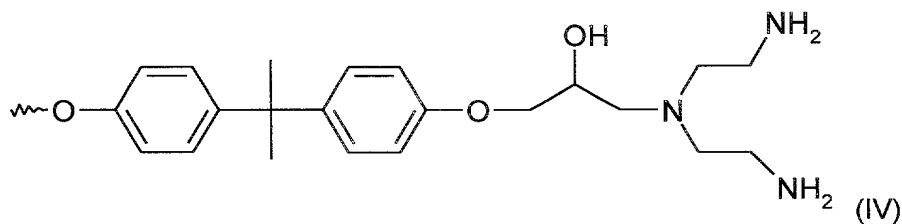
For purposes of the present invention, the amines from which the pendant and/or terminal amino groups are derived comprise primary and/or secondary amine groups such that the active hydrogens of said amines will be consumed by reaction

with the at least partially blocked aliphatic polyisocyanate curing agent (2) to form urea groups or linkages during the curing reaction. The urea groups formed during the curing reaction appear to have no significant negative influence on photodegradation resistance of the cured electrodeposited coating where the subsequently applied top coat has at least 0.1 percent light transmission as measured at 400 nanometers.

In one embodiment of the present invention, a polyepoxide polymer can be "defunctionalized" with an excess of ammonia, yielding a polymer comprising one or more of the following structural units (III). Cationic salt groups subsequently can be formed by admixing such a polymer with a suitable solubilizing acid to promote dispersion in water.



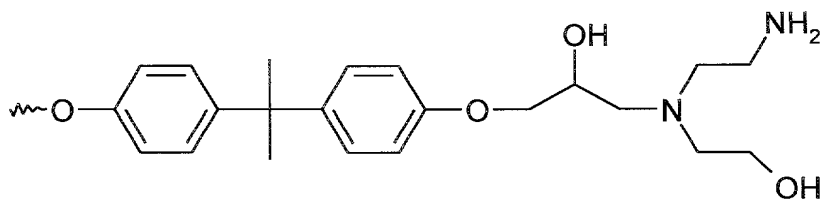
In an alternative embodiment of the present invention, the cationic polymer (1) can comprise a polyepoxide polymer having pendant and/or terminal amino groups comprising primary amine groups from which cationic amine salts can be formed. Such a polymer can be prepared, for example, by reacting diethylene triamine bis-ketamine with an epoxy group containing polymer, followed by hydrolysis to decompose the ketimine. Such a polymer can comprise one or more of the following structural units (IV):



It was surprising to find that, despite the presence of the tertiary nitrogen in this structural unit, electrodeposited compositions comprising such polymers exhibit improved photodegradation resistance. Without intending to be bound by theory, it is believed that this is due to the formation during the cure reaction with the

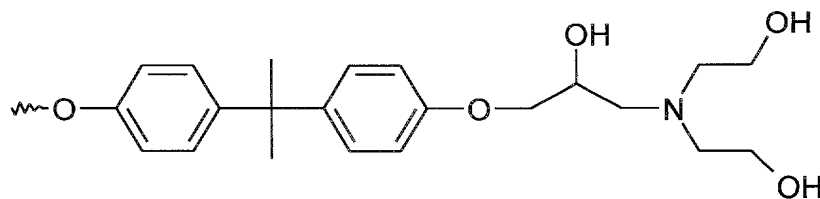
polyisocyanate curing agent of two strong electron-withdrawing groups (in this case, urea groups) bonded in the beta-position relative to the tertiary nitrogen.

Likewise, it was found that polymers comprising other structural units having isocyanate-reactive groups in the beta-position relative to the nitrogen atom also can exhibit similar photodegradation resistance. Such polymers can comprise, for example, the following structural units (V) and (VI):



(V)

or



(VI)

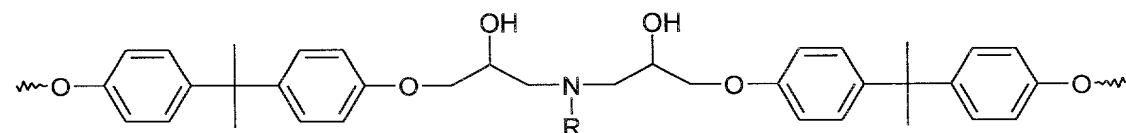
Upon reaction of polymers having one or more of the structural units (VI) with the polyisocyanate curing agent (2), electron-withdrawing urethane groups are formed at the beta-position relative to the tertiary nitrogen atoms which are derived from the pendant and/or terminal amino groups. Likewise, upon reaction of polymers having one or more of the structural units (V) with the polyisocyanate curing agent (2), electron-withdrawing urethane and urea groups are formed at the beta-position relative to the tertiary nitrogen atoms derived from the pendant and/or terminal amino groups.

As used herein, in the specification and in the claims, by "electron-withdrawing group" is meant a group (e.g., a urethane or urea group) that tends to draw electrons or electronegative charge from the amine nitrogen atom, thereby rendering the amine nitrogen less basic. Such electron-withdrawing groups can be derived from the reaction of the polyisocyanate curing agent (2) with the hydroxyl



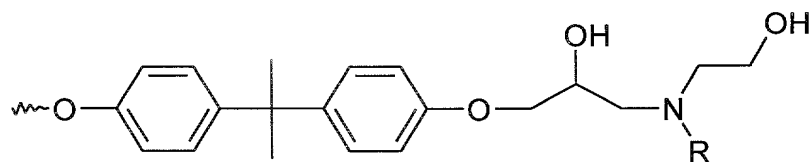
and/or amino groups, represented by X and Y in structure (II) above, which are pendant and/or terminal from the resin (1). Moreover, it should be understood that for purposes of the present invention, the urethane groups derived from the reaction of the polyisocyanate curing agent and the hydroxyl groups along the polymer backbone, and/or the secondary hydroxyl groups which are formed upon the ring opening of an epoxy group, are not intended to be within the meaning of the term "electron-withdrawing group(s)".

It has been found that polymers comprising primarily structural units such as structural units (VII) and/or (VIII) below, where R represents an unsubstituted alkyl group, exhibit significantly poorer photodegradation resistance as compared to those polymers discussed immediately above. Without intending to be bound by theory, it is believed that the poorer photodegradation resistance of such polymers comprising primarily structural units (VII) and/or (VIII) can be attributed to the fact that the basic nitrogens are present in the backbone of the polymer (and are not pendant and/or terminal with respect to the polymer backbone) and/or do not react with the polyisocyanate curing agent to generate two electron-withdrawing groups in the beta-position relative to the basic amine group.



(VII)

and/or



(VIII)

It can be inferred by those skilled in the art from the generally poorer cure response of cationic epoxies containing a preponderance of structural units (VII) and (VIII), that the hydroxyl groups beta to phenoxy groups on the backbone of (VII) and near the end of structural unit (VIII) do not effectively participate in cure, i.e. they are not completely converted to electron-withdrawing urethane groups during the curing step. Also, it should here be noted that the degree of consumption of basic nitrogen by reaction with the polyisocyanate curing agent can be measured by titration of the cryogenically ground electrodepositable composition after the curing step as described above.

If desired, a minor amount of the polymer(s) having the structural units (VII) and/or (VIII) can be included in the electrodepositable coating compositions of the present invention, provided that such polymers are not present in an amount sufficient to negatively affect photodegradation resistance of the cured electrodeposited coating.

The active hydrogen-containing, terminal amino group-containing polymer is rendered cationic and water dispersible by at least partial neutralization with an acid. Suitable acids include organic and inorganic acids such as formic acid, acetic acid, lactic acid, phosphoric acid, dimethylolpropionic acid, and sulfamic acid. Mixtures of acids can be used. The extent of neutralization varies with the particular reaction product involved. However, sufficient acid should be used to disperse the electrodepositable composition in water. Typically, the amount of acid used provides at least 30 percent of the total theoretical neutralization. Excess acid may also be used beyond the amount required for 100 percent total theoretical neutralization.

The extent of cationic salt group formation should be such that when the polymer is mixed with an aqueous medium and the other ingredients, a stable dispersion of the electrodepositable composition will form. By "stable dispersion" is meant one that does not settle or is easily redispersible if some settling occurs. Moreover, the dispersion should be of sufficient cationic character that the dispersed particles will migrate toward and electrodeposit on a cathode when an electrical potential is set up between an anode and a cathode immersed in the aqueous dispersion.

Generally, the cationic polymer is ungelled and contains from about 0.1 to 3.0, preferably from about 0.1 to 0.7 millequivalents of cationic salt group per gram of polymer solids.

The active hydrogens associated with the cationic polymer include any active hydrogens which are reactive with isocyanates within the temperature range of about 93°C to 204 °C, preferably about 121°C to 177°C. Typically, the active hydrogens are selected from the group consisting of hydroxyl and primary and secondary amino, including mixed groups such as hydroxyl and primary amino. Preferably, the polymer will have an active hydrogen content of about 1.7 to 10 millequivalents, more preferably about 2.0 to 5 millequivalents of active hydrogen per gram of polymer solids.

The cationic salt group-containing polymer can be present in the electrodepositable composition used in the processes of the present invention in an amount ranging from 20 to 80 percent, often from 30 to 75 percent by weight, and typically from 50 to 70 percent by weight based on the total combined weight of resin solids of the cationic salt group-containing polymer and the curing agent.

As mentioned above, the resinous phase of the electrodepositable coating composition further comprises (2) a curing agent adapted to react with the active hydrogen groups of the cationic electrodepositable resin (1) described immediately above. In one embodiment of the present invention, the curing agent (2) comprises one or more at least partially blocked aliphatic polyisocyanates. In this embodiment, a minor amount (i.e. less than 10, preferably less than 5 weight percent of total resin solids of the curing agent present in the composition) of aromatic polyisocyanate can be included, provided that the aromatic polyisocyanate is not present in an amount sufficient to deleteriously affect the photodegradation resistance of the cured electrodeposited composition.

The curing agents employed in cationic electrodeposition compositions of the present invention typically are blocked aliphatic polyisocyanates. The aliphatic polyisocyanates can be fully blocked as described in U.S. Patent No. 3,984,299 column 1 lines 1 to 68, column 2 and column 3 lines 1 to 15, or partially blocked and reacted with the polymer backbone as described in U. S. Patent No. 3,947,338 column 2 lines 65 to 68, column 3 and column 4 lines 1 to 30. By "blocked" is meant that the isocyanate groups have been reacted with a compound such that the resultant blocked isocyanate group is stable to active hydrogens at ambient temperature but reactive with active hydrogens in the film forming polymer at elevated temperatures usually between 90°C and 200°C. In one embodiment of the

present invention, the polyisocyanate curing agent is a fully blocked polyisocyanate with substantially no free isocyanate groups.

Diisocyanates typically are used, although higher polyisocyanates can be used in lieu of or in combination with diisocyanates. Examples of aliphatic polyisocyanates suitable for use as curing agents include cycloaliphatic and araliphatic polyisocyanates such as 1,6-hexamethylene diisocyanate, isophorone diisocyanate, bis-(isocyanatocyclohexyl)methane, polymeric 1,6-hexamethylene diisocyanate, trimerized isophorone diisocyanate, norbornane diisocyanate and mixtures thereof. In a particular embodiment of the present invention, the curing agent (2) comprises a fully blocked polyisocyanate selected from a polymeric 1,6-hexamethylene diisocyanate, isophorone diisocyanate, and mixtures thereof. In another embodiment of the present invention the polyisocyanate curing agent comprises a fully blocked trimer of hexamethylene diisocyanate available as Desmodur N3300® from Bayer Corporation.

In one embodiment of the present invention, the polyisocyanate curing agent (2) is at least partially blocked with at least one blocking agent selected from a 1,2-alkane diol, for example 1,2-propanediol, a 1,3-alkane diol, for example 1,3-butanediol, a benzylic alcohol, for example, benzyl alcohol, an allylic alcohol, for example, allyl alcohol, caprolactam, a dialkylamine, for example dibutylamine, and mixtures thereof. In a further embodiment of the present invention, the polyisocyanate curing agent (2) is at least partially blocked with at least one 1,2-alkane diol having three or more carbon atoms, for example 1,2-butanediol.

If desired, the blocking agent can further comprise minor amounts of other well known blocking agents such as aliphatic, cycloaliphatic, or aromatic alkyl monoalcohol or phenolic compound, including, for example, lower aliphatic alcohols such as methanol, ethanol, and n-butanol; cycloaliphatic alcohols such as cyclohexanol; aromatic-alkyl alcohols such as phenyl carbinol and methylphenyl carbinol; and phenolic compounds such as phenol itself and substituted phenols wherein the substituents do not affect coating operations, such as cresol and nitrophenol. Glycol ethers and glycol amines may also be used as blocking agents. Suitable glycol ethers include ethylene glycol butyl ether, diethylene glycol butyl ether, ethylene glycol methyl ether and propylene glycol methyl ether. Other suitable blocking agents include oximes such as methyl ethyl ketoxime, acetone oxime and cyclohexanone oxime. As mentioned above, these conventional blocking agents can

be used in minor amounts provided that they are not present in amounts sufficient to deleteriously affect photodegradation resistance of the cured electrodeposited coating.

The at least partially blocked polyisocyanate curing agent (2) can be present in the electrodepositable composition used in the processes of the present invention in an amount ranging from 80 to 20 percent, often from 75 to 30, and typically from 70 to 50 percent by weight, based on the total combined weight of resin solids of the cationic salt group-containing polymer (1) and the curing agent (2).

As mentioned above, the present invention also is directed to an "alternative process" for coating any of the metal substrates described in detail above comprising: (a) electrophoretically depositing on at least a portion of the substrate a curable, electrodepositable coating composition described below; (b) heating the substrate to a temperature of 250°F to 400°F (121.1°C to 204.4°C) for a time sufficient to effect cure of the electrodepositable composition; (c) applying directly to the electrodepositable composition one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions to form a top coat thereover; and (d) heating the coated substrate to a temperature and for a time sufficient to effect cure of the top coating composition(s).

This "alternative process" can include one or more optional steps, as outlined below: (a) optionally forming a metal object from the substrate; (b) optionally cleaning the substrate with an alkaline and/or acidic cleaner such as any of those described above; (c) optionally pretreating the substrate with a solution selected from the group consisting of a metal phosphate solution, an aqueous solution containing at least one Group IIIB or IVB metal, an organophosphate solution, an organophosphonate solution, and combinations thereof, suitable examples of which are described above; (d) optionally rinsing the substrate with water; (e) electrophoretically depositing on the substrate the curable, electrodepositable coating composition described below; (f) heating the substrate to a temperature ranging from 250°F to 400°F (121.1°C to 204.4°C) for a time sufficient to effect cure of the electrodepositable composition; (g) applying directly to the electrodepositable composition one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions to form a top coat thereover; and (h) heating the coated substrate to a temperature and for a time sufficient to effect cure of the top coating composition(s).

Note that the order of the alternative process steps (a) through (h) can be altered with the same results and without departing from the scope of the invention. Also, additional water rinsing steps can be added as necessary.

Also provided is a curable, electrodepositable coating composition used in the above "alternative process". This composition comprises: (1) an active hydrogen-containing, cationic salt group-containing resin electrodepositable on a cathode, derived from a polyglycidyl ether of a polyhydric phenol that is essentially free of aliphatic carbon atoms to which are bonded more than one aromatic group; and (2) an at least partially blocked polyisocyanate curing agent essentially free of isocyanato groups or blocked isocyanato groups to which are bonded aromatic groups.

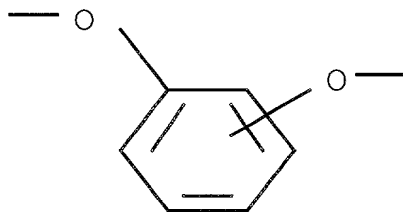
The curable electrodepositable coating composition for use in the "alternative processes" of the present invention typically comprises an amine salt group-containing resin (1) in conjunction with an at least partially blocked polyisocyanate curing agent (2). In a particular embodiment, this composition comprises a cationic polyepoxide resin which comprises a chain-extended polyglycidyl ether of a polyhydric phenol having cationic salt groups and active hydrogen groups selected from aliphatic hydroxyl and primary and secondary amino groups.

Such a chain-extended polyepoxide can be prepared by reacting together the polyepoxide and a polyhydroxyl or polycarboxyl group-containing material neat, or in the presence of an inert organic solvent such as a ketone, including methyl isobutyl ketone and methyl amyl ketone, aromatic solvents such as toluene and xylene, and glycol ethers such as the dimethyl ether of diethylene glycol. The reaction usually is conducted at a temperature ranging from 80°C to 160°C for 30 to 180 minutes, until an epoxy group-containing resinous reaction product is obtained. In general, the epoxide equivalent weight of such polyepoxides will range from 100 to 2000, typically from 180 to 500. The epoxy compounds may be saturated or unsaturated, cyclic or acyclic, aliphatic, alicyclic, aromatic or heterocyclic. They may contain substituents such as halogen, hydroxyl, and ether groups.

Examples of polyepoxides suitable for use in the alternative compositions are those having a 1,2-epoxy equivalency greater than one and preferably about two; that is, polyepoxides that have on average two epoxide groups per molecule. Suitable polyepoxides are polyglycidyl ethers of polyhydric phenols that are essentially free of aliphatic carbon atoms to which are bonded more than one

aromatic group. In one alternative embodiment, such polyepoxides comprise polyglycidyl ethers of polyhydric phenols selected from the group consisting of resorcinol, hydroquinone, catechol, and mixtures thereof. In another embodiment, these polyepoxides comprise polyglycidyl ethers of polyhydric phenols selected from resorcinol, catechol and mixtures thereof. These polyglycidyl ethers of polyhydric phenols can be produced by etherification of polyhydric phenols with an epihalohydrin or dihalohydrin such as epichlorohydrin or dichlorohydrin in the presence of alkali.

In the electrodepositable compositions for use in the alternative processes of the present invention, the cationic salt group-containing resin comprises at least 16 percent by weight, typically least 30 percent by weight, based on the total weight of resin solids, of a functional group having the following structure:



Examples of polyhydroxyl group-containing materials used to chain extend or increase the molecular weight of the polyepoxide (i. e., through hydroxyl-epoxy reaction) include any of the polyhydric phenols listed above. Other polyols can also be used in chain extension. Examples of cyclic polyols include alicyclic polyols, particularly cycloaliphatic polyols such as 1,2-cyclohexane diol, 1,4-cyclohexane diol, 2,2-bis(4-hydroxycyclohexyl)propane, 1,1-bis(4-hydroxycyclohexyl)ethane, 2-methyl-1,1-bis(4-hydroxycyclohexyl)propane, 2,2-bis(4-hydroxy-3-tertiarybutylcyclohexyl)propane, 1,3-bis(hydroxymethyl)cyclohexane and 1,2-bis(hydroxymethyl)cyclohexane. Examples of aliphatic polyols include, inter alia, trimethylpentanediol and neopentyl glycol. Polymeric polyols suitable for chain extension include polyester polyols such as those described in U. S. Patent No. 4,148,772; and urethane diols such as those described in U. S. Patent No. 4,931,157, with the proviso that the polyols described in these patents should be essentially free of aliphatic carbon atoms to which are bonded more than one aromatic group. Mixtures of alcoholic hydroxyl group-containing materials and phenolic hydroxyl group-containing materials may also be used.

The equivalent ratio of reactants; i. e., epoxy:polyhydroxyl group-containing material during chain extension typically is from 1.00:0.75 to 1.00:2.00. The chain extension of such polyepoxides can also be performed using a polycarboxylic acid material, most often a dicarboxylic acid. Useful dicarboxylic acids include acids having the general formula:  $\text{HOOC}-\text{R}-\text{COOH}$ , where R is a divalent moiety that is substantially unreactive with the polyepoxide. R can be a straight chained or a branched alkylene or alkylidene moiety normally containing from 2 to 42 carbon atoms. Some examples of suitable dicarboxylic acids include cyclohexanedicarboxylic acid, which is preferred, adipic acid, 3,3-dimethylpentanedioic acid, benzenedicarboxylic acid, phenylenediethanoic acid, naphthalenedicarboxylic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid and the like. It should be understood that dicarboxylic acids of the above general formula where R is a moiety of less than 4 carbon atoms can include, for example, oxalic acid, malonic acid, succinic acid, and glutaric acid, but these acids are less preferred. Additional suitable dicarboxylic acids include substantially saturated acyclic, aliphatic dimer acids formed by the dimerization reaction of fatty acids having from 4 to 22 carbon atoms and a terminal carboxyl group (forming dimer acids having from 8 to 44 carbon atoms). Dimer acids are well known in the art and are commercially available from Emery Industries, Inc. under the name EMPOL®. Dicarboxylic acids can be formed as reaction products of anhydrides and diols or diamines at reaction conditions and techniques known to those skilled in the art for the particular reactants. Diols can include polytetramethylene glycols, polycaprolactones, polypropylene glycols, polyethylene glycols, and the like. Suitable anhydrides include maleic, phthalic, hexahydrophthalic, tetrahydrophthalic and the like. Additionally, dicarboxylic acids formed by the reaction of an anhydride and a diamine can be used. Dicarboxylic acids formed by the reaction of a polyoxyalkylenediamine such as polyoxypropylenediamine, commercially available from Huntsman Chemical Company under the name JEFFAMINE®, with an anhydride like those listed above can be used.

Typically, the amount of dicarboxylic acid used to chain extend the polyepoxide is sufficient to provide from 0.05 to 0.6, often from 0.2 to 0.4 acid groups per epoxide group. This reaction normally is carried out at between 80°C and 175°C.



Materials having mixed hydroxyl and carboxyl functionality, such as 2-hydroxypivalic acid, are also suitable for use as chain extending agents. Materials having mixed hydroxyl/amino and amino/carboxyl functionality may also be used, some of which are further described below.

5 The chain-extended polyepoxides can have number average molecular weights ranging from 1000 to 3000, typically from 1700 to 2600. Epoxy group-containing acrylic polymers can also be used. One particular suitable polyepoxide is a cycloaliphatic diepoxide available as EPON X1510® from Shell Oil and Chemical Company, chain extended with a material selected from resorcinol, catechol and  
10 mixtures thereof.

Any of the previously described acrylic, polyester, polyurethane and polyepoxide resins also can be used in conjunction with the polyepoxides described immediately above (i.e., those used in the alternative compositions).

As mentioned above, the compositions used in the alternative processes of  
15 the present invention comprise a resin, such as the polyepoxides described immediately above, having cationic salt groups. The cationic salt groups can be incorporated into the resin by reacting the epoxy group-containing resinous reaction product prepared as described above with a material capable of forming cationic salt groups. Such a material is reactive with epoxy groups and can be acidified before,  
20 during, or after reaction with the epoxy groups to form cationic salt groups. Examples of suitable materials include amines such as primary or secondary amines which can be acidified after reaction with the epoxy groups to form amine salt groups, or tertiary amines which can be acidified prior to reaction with the epoxy groups and which after reaction with the epoxy groups form quaternary ammonium salt groups.  
25 Examples of other suitable materials include sulfides, which can be mixed with acid prior to reaction with the epoxy groups and form ternary sulfonium salt groups upon subsequent reaction with the epoxy groups.

When amines are used to form cationic salt groups, monoamines, typically hydroxyl-containing amines, are employed. Polyamines may be used but are not  
30 recommended because of a tendency to gel the resin.

In one embodiment of the invention, the cationic salt group-containing resin (used in the alternative electrodepositable compositions) contains amine salt groups which are derived from an amine containing a nitrogen atom to which is bonded at least one, preferably two, alkyl groups having a hetero atom in a beta- position

relative to the nitrogen atom. A hetero atom is a non-carbon or non-hydrogen atom, typically oxygen, nitrogen, or sulfur.

Hydroxyl-containing amines, when used for this purpose, can impart the resin with amine groups comprising a nitrogen atom to which is bonded at least one alkyl group having a hetero atom in a beta- position relative to the nitrogen atom.

Examples of hydroxyl-containing amines are alkanolamines, dialkanolamines, alkyl alkanolamines, and aralkyl alkanolamines containing from 1 to 18 carbon atoms, typically from 1 to 6 carbon atoms in each of the alkanol, alkyl and aryl groups. Specific examples include ethanolamine, N-methylethanolamine, diethanolamine, N-phenylethanolamine, N,N-dimethylethanolamine, N-methyldiethanolamine, and N-(2-hydroxyethyl)-piperazine. In one particular alternative embodiment of the present invention amines are selected from the group consisting of diethylenetriamine, diethylenetriamine bisketamine, aminopropyldiethanolamine, aminopropylmorpholine, N-(2-aminoethyl)-morpholine, and mixtures thereof.

Minor amounts of amines such as mono, di, and trialkylamines and mixed aryl-alkyl amines which do not contain hydroxyl groups, or amines substituted with groups other than hydroxyl which do not negatively affect the reaction between the amine and the epoxy also can be used. Specific examples include ethylamine, methylethylamine, triethylamine, N-benzyl dimethylamine, dicocoamine and N,N-dimethylcyclohexylamine.

Mixtures of the above mentioned amines also may be used. Note that for purposes of this alternative embodiment of the invention, all of the amines mentioned above as suitable for use as cationic salt group formers may also be used to chain extend the polyepoxide prior to salt group formation.

The reaction of a primary and/or secondary amine with the polyepoxide takes place upon mixing of the amine and polyepoxide. The amine may be added to the polyepoxide or vice versa. The reaction can be conducted neat, or in the presence of, a suitable solvent such as methyl isobutyl ketone, xylene, or 1-methoxy-2-propanol. The reaction is generally exothermic and cooling may be desired.

However, heating to a moderate temperature of about 50°C to 150°C may be done to hasten the reaction.

The reaction product of the primary and/or secondary amine and the polyepoxide is made cationic and water dispersible by at least partial neutralization with an acid. Suitable acids include any of the organic and inorganic neutralizing

acids mentioned above. The extent of neutralization varies with the particular reaction product involved. However, sufficient acid should be used to disperse the electrodepositable composition in water. Typically, the amount of acid used provides at least 20 percent of all of the total theoretical neutralization. Excess acid also may  
5 be used beyond the amount required for 100 percent total theoretical neutralization.

In the reaction of a tertiary amine with a polyepoxide, the tertiary amine can be prereacted with the neutralizing acid to form the amine salt and then the amine salt reacted with the polyepoxide to form a quaternary salt group-containing resin. The reaction is conducted by mixing the amine salt with the polyepoxide in water.  
10 Typically the water is present in an amount ranging from about 1.75 to about 20 percent by weight based on total reaction mixture solids.

In forming the quaternary ammonium salt group-containing resin, the reaction temperature can be varied from the lowest temperature at which the reaction will proceed, generally at or slightly above room temperature, to a maximum temperature  
15 of about 100°C (at atmospheric pressure). At higher pressures, higher reaction temperatures may be used. Preferably the reaction temperature is in the range of about 60°C to 100°C. Solvents such as a sterically hindered ester, ether, or sterically hindered ketone may be used, but their use is not necessary.

In addition to the primary, secondary, and tertiary amines disclosed above, a  
20 portion of the amine that is reacted with the polyepoxide can be a ketimine of a polyamine, such as those described above.

In addition to resins containing amine salts and quaternary ammonium salt groups, cationic resins containing ternary sulfonium groups may be used in forming the cationic polyepoxide used in this alternative embodiment. Examples of these  
25 resins and their method of preparation are described in U. S. Patent Nos. 3,793,278 to DeBona and 3,959,106 to Bosso et al., incorporated herein by reference.

Generally, the cationic resin is ungelled and contains from about 0.1 to 3.0, preferably from about 0.1 to 0.7 millequivalents of cationic salt group per gram of resin solids. Typically, the polyepoxide will have an active hydrogen content of 1.7 to  
30 10 millequivalents, and often 2.0 to 5 millequivalents of active hydrogen per gram of resin solids.

The cationic salt group-containing resin can be present in the alternative composition of the present invention in an amount ranging from 20 to 80 percent, often 30 to 75 percent by weight, and typically 40 to 70 percent by weight based on

the total combined weight of resin solids of the cationic salt group-containing resin (1) and the curing agent (2).

The polyisocyanate curing agent used in the alternative compositions of the present invention can be at least partially blocked, and typically is a fully blocked polyisocyanate with substantially no free isocyanate groups. The polyisocyanate can be an aliphatic or an aromatic polyisocyanate, or a mixture of the two, however, the curing agent is essentially free of isocyanato groups or blocked isocyanato groups to which are bonded aromatic groups. That is, for purposes of the alternative compositions, any aromatic groups present in the curing agent are not directly bonded to the isocyanato groups. Diisocyanates are most often employed, although higher polyisocyanates can be used in lieu of or in combination with diisocyanates.

Examples of suitable aliphatic diisocyanates include any of the previously described aliphatic polyisocyanates. Examples of suitable aralkyl diisocyanates are meta-xylylene diisocyanate and  $\alpha \alpha' \alpha' \alpha'$  tetramethylmeta-xylylene diisocyanate. A preferred polyisocyanate is a fully blocked trimer of hexamethylene diisocyanate available as DESMODUR N3300 from Bayer Corporation.

Isocyanate prepolymers, for example, reaction products of polyisocyanates with polyols such as neopentyl glycol and trimethylol propane or with polymeric polyols such as polycaprolactone diols and triols (NCO/OH equivalent ratio greater than one) can also be used.

For purposes of the alternative embodiment of the present invention, any suitable aliphatic, cycloaliphatic, or aromatic alkyl monoalcohol or phenolic compound may be used as a capping agent for the polyisocyanate including, for example, lower aliphatic alcohols such as methanol, ethanol, and n-butanol; cycloaliphatic alcohols such as cyclohexanol; aromatic-alkyl alcohols such as phenyl carbinol and methylphenyl carbinol; and phenolic compounds such as phenol itself and substituted phenols wherein the substituents do not affect coating operations, such as cresol and nitrophenol. Glycol ethers may also be used as capping agents. Suitable glycol ethers include ethylene glycol butyl ether, diethylene glycol butyl ether, ethylene glycol methyl ether and propylene glycol methyl ether. Diethylene glycol butyl ether is preferred among the glycol ethers.

Other suitable capping agents include oximes such as methyl ethyl ketoxime, acetone oxime and cyclohexanone oxime, lactams such as epsilon-caprolactam, and secondary amines such as dibutyl amine.

The polyisocyanate curing agent can be present in the alternative composition of the present invention in an amount of 20 to 80 percent, usually 30 to 75 percent by weight, typically 50 to 70 percent by weight based on the total combined weight of resin solids of the cationic salt group-containing resin (1) and the curing agent (2).

This compositions of the alternative embodiment of the present invention, when applied to a substrate and properly cured, then subjected to corrosion testing such as a standard ASTM B117 salt spray test or a cyclic test such as GM Engineering Standard 9540P, Method B, will have no more scribe corrosion than exhibited by suitable controls containing aromatic isocyanates and/or Bisphenol A based aromatic polyepoxides. When top coated with a transparent base coat and /or clear coat composition having greater than 50% light transmission measured at 400 nanometers wave length, it will endure at least 1500 hours xenon arc accelerated weathering as per SAE J1960 without substantial degradation. Any of the previously described electrodepositable coating compositions can further comprise at least one source of a metal selected from rare earth metals, yttrium, bismuth, zirconium, tungsten, and mixtures thereof. The at least one source of metal typically is present in the electrodepositable composition in an amount of 0.005 to 5 percent by weight metal, based on the total weight of resin solids in the coating composition. Yttrium typically is employed.

Both soluble and insoluble yttrium compounds may serve as the source of yttrium in the electrodepositable composition used in the process of the present invention. Examples of yttrium sources suitable for use in the electrodepositable composition are soluble organic and inorganic yttrium salts such as yttrium acetate, yttrium chloride, yttrium formate, yttrium carbonate, yttrium sulfamate, yttrium lactate and yttrium nitrate. When the yttrium is to be added to the composition as an aqueous solution, yttrium nitrate, a readily available yttrium compound, is a preferred yttrium source. Other suitable yttrium compounds are organic and inorganic yttrium compounds such as yttrium oxide, yttrium bromide, yttrium hydroxide, yttrium molybdate, yttrium sulfate, yttrium silicate, and yttrium oxalate. Organoyttrium complexes and yttrium metal can also be used. When the yttrium is to be incorporated into the composition as a component in a pigment paste, yttrium oxide is the preferred source of yttrium.

Suitable rare earth metal compounds include soluble, insoluble, organic, and inorganic salts of rare earth metals, such as acetates, oxalates, formates, lactates, oxides, hydroxides, molybdates, etc., of the rare earth metals.

There are various methods by which the yttrium, bismuth, zirconium, tungsten, or rare earth metal compound can be incorporated into any of the electrodepositable compositions used in any of the processes of the present invention. A soluble compound may be added "neat," that is, added directly to the composition without prior blending or reacting with other components. Alternatively, a soluble compound can be added to the predispersed clear polymer feed which may include the cationic polymer, the curing agent and/or any other non-pigmented component. Preferably, a soluble compound is added "neat". Insoluble compounds and/or metal pigments, on the other hand, are preferably pre-blended with a pigment paste component prior to the incorporation of the paste to the electrodepositable composition.

Any of the above described electrodepositable compositions used in any of the processes of the present invention can contain yttrium, bismuth, zirconium, tungsten, or a rare earth metal as the sole corrosion inhibiting inorganic component or can be supplemented with other corrosion inhibiting inorganic or organic components such as calcium. In one embodiment of the present invention, the electrodepositable coating composition used in the processes and photodegradation resistant coatings and multi-layer composite coatings of the present invention is substantially free of heavy metals such as lead.

Any of the previously described electrodepositable compositions of the present invention can further comprise a hindered amine light stabilizer for added UV degradation resistance, but it is not required. Such hindered amine light stabilizers include those disclosed in U. S. Patent No. 5,260,135. When used, these materials can be present in the electrodepositable composition in an amount of 0.1 to 2 percent by weight, based on the total weight of polymer solids in the electrodepositable composition.

The compositions when used as an electrodeposition bath in any of the previously described processes of the present invention have a polymer solids content usually within the range of about 5 to 25 percent by weight based on total weight of the electrodeposition bath.

Besides water, the aqueous medium of the electrodeposition bath may contain a coalescing solvent. Useful coalescing solvents include hydrocarbons, alcohols, esters, ethers and ketones. The preferred coalescing solvents include alcohols, polyols and ketones. Specific coalescing solvents include isopropanol, butanol, 2-ethylhexanol, isophorone, 2-methoxypentanone, ethylene and propylene glycol and the monoethyl, monobutyl and monohexyl ethers of ethylene glycol. The amount of coalescing solvent is generally between about 0.01 and 25 percent and when used, preferably from about 0.05 to about 5 percent by weight based on total weight of the aqueous medium.

As mentioned above, a pigment composition and other optional additives such as surfactants, wetting agents or catalyst can be included in the electrodeposition bath. The pigment composition may be of the conventional type comprising inorganic pigments, for example, iron oxides, china clay, carbon black, coal dust, titanium dioxide, talc, barium sulfate, as well as organic color pigments such as phthalocyanine green and the like. The pigment content of the dispersion is usually expressed as a pigment-to-polymer ratio. In the practice of the invention, when pigment is employed, the pigment-to-polymer ratio is usually within the range of about 0.02 to 1:1. The other additives mentioned above are usually in the dispersion in amounts of about 0.01 to 3 percent by weight based on weight of polymer solids.

All of the electrodepositable coating compositions of the present invention are in the form of an aqueous dispersion. The term "dispersion" is believed to be a two-phase transparent, translucent or opaque resinous system in which the resin is in the dispersed phase and the water is in the continuous phase. The average particle size of the resinous phase is generally less than 1.0, usually less than 0.5 microns, and typically less than 0.15 micron.

The concentration of the resinous phase in the aqueous medium is at least 1 and usually from 2 to 60 percent by weight based on total weight of the aqueous dispersion. When the compositions of the present invention are in the form of resin concentrates, they generally have a resin solids content of 20 to 60 percent by weight based on weight of the aqueous dispersion.

The previously described curable electrodepositable coating compositions of the present invention typically are supplied as two components: (1) a clear resin feed, which includes, generally, active hydrogen-containing, cationic polymer, i.e., the main film-forming polymer, the at least partially blocked polyisocyanate curing agent, and

any additional water-dispersible, non-pigmented components; and (2) a pigment paste (described above), which, generally, includes one or more pigments, a water-dispersible grind resin which can be the same or different from the main-film forming polymer, and, optionally, additives such as catalysts, and wetting or dispersing aids.

- 5 An electrodeposition bath is prepared by dispersing components (1) and (2) in an aqueous medium which comprises water and, usually, coalescing solvents. Alternatively, the electrodepositable compositions of the present invention can be supplied as one component compositions.

Generally, as aforementioned, in the process of electrodeposition, the metal  
10 substrate being coated, serving as a cathode, and an electrically conductive anode are placed in contact with the cationic electrodepositable composition. Upon passage of an electric current between the cathode and the anode while they are in contact with the electrodepositable composition, an adherent film of the electrodepositable composition will deposit in a substantially continuous manner on  
15 the electroconductive substrate.

In one embodiment, the present invention is directed to an improved process for forming a photodegradation-resistant multi-layer coating on an electrically conductive substrate comprising (a) electrophoretically depositing on the substrate any of the aqueous, curable electrodepositable coating compositions described  
20 above to form an electrodeposited coating over at least a portion of the substrate, the substrate serving as a cathode in an electrical circuit comprising the cathode and an anode, the cathode and the anode being immersed in the aqueous electrodepositable coating composition, wherein electric current is passed between the cathode and the anode to cause the coating to be electrodeposited over at least  
25 a portion of the substrate: (b) heating the coated substrate at a temperature and for a time sufficient to cure the electrodeposited coating on the substrate; (c) applying directly to the cured electrodeposited coating one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions to form a top coat over at least a portion of the cured electrodeposited coating; and (d) heating the  
30 coated substrate of step (c) to a temperature and for a time sufficient to cure the top coat, the cured top coat having at least 0.1 percent light transmission as measured at 400 nanometers. The improvement comprises the inclusion in the circuit of a non-ferrous anode, for example, anodes comprised of ruthenium oxide and carbon rods.



In most conventional cationic electrodeposition bath systems, the anode(s) are comprised of a ferrous material, for example, stainless steel. A typical cationic bath has an acidic pH ranging from 4.0 to 7.0, and often from 5.0 to 6.0. However, in a typical electrodeposition bath system, the anolyte (i.e., the bath solution in the immediate area of the anode) can have a pH as low as 3.0 or less due to the concentration of acid at or near the anode. At these strongly acidic pH ranges, the ferrous anode can degrade, thereby releasing soluble iron into the bath. By "soluble iron" is meant  $\text{Fe}^{+2}$  or  $\text{Fe}^{+3}$  ions derived from iron salts which are at least partially soluble in water. During the electrodeposition process, the soluble iron is electrodeposited along with the resinous binder and is present in the cured electrodeposited coating. It has been found that the presence of iron in soluble form can contribute to interlayer delamination of subsequently applied top coat layers from the cured electrodeposited coating layer upon weathering exposure. In view of the foregoing, it is desirable that the electrodepositable coating composition of the present invention, when in the form of an electrodeposition bath, comprises less than 10 parts per million, typically less than 1 part per million of soluble iron. This can be accomplished by the inclusion in the circuit of a non-ferrous anode.

Once the above-described electrodepositable coating composition is electrodeposited over at least a portion of the electroconductive substrate, the coated substrate is heated to a temperature and for a time sufficient to cure the electrodeposited coating on the substrate. The coated substrate can be heated to a temperature ranging from 250° to 450°F (121.1° to 232.2°C), often from 250° to 400°F (121.1° to 204.4°C), and typically from 300° to 360° (148.9° to 180°C). The curing time can be dependent upon the curing temperature as well as other variables, for example, film thickness of the electrodeposited coating, level and type of catalyst present in the composition and the like. For purposes of the present invention, all that is necessary is that the time be sufficient to effect cure of the electrodeposited coating on the substrate. For example, the curing time can range from 10 minutes to 60 minutes, and typically from 10 to 30 minutes.

In one embodiment of the present invention, the coated substrate is heated to a temperature of 360°F (180°C) or less for a time sufficient to effect cure of the electrodeposited coating on the substrate. The thickness of the resultant cured electrodeposited coating usually ranges from 15 to 50 microns.

In another embodiment, the present invention is directed to a process wherein any of the above-described electrodepositable coating compositions can be electrophoretically applied to an electroconductive substrate as in step (a), and heated in an atmosphere having 5 parts per million or less, typically 1 part per million or less, of nitrogen oxides (NO<sub>x</sub>) to a temperature and for a time sufficient to cure the electrodeposited coating on the substrate as described above. The presence of NO<sub>x</sub> in the curing ovens can create an oxidizing atmosphere which can result in interlayer delamination between the cured electrodeposited coating and any subsequently applied top coats upon weathering exposure.

Nitrogen oxides can be formed during combustion of a hydrocarbon fuel, such as natural gas used to fuel gas-fired ovens. Nitrogen oxides form as a result of two oxidation mechanisms: (1) reaction of nitrogen in the combustion air with excess oxygen (referred to as thermal  $\text{NO}_x$ ) and (2) reaction of nitrogen that is chemically bound in the fuel (referred to as fuel  $\text{NO}_x$ ). In addition, minor amounts of  $\text{NO}_x$  are formed through complex interaction of molecular nitrogen with hydrocarbons in the early phase of the flame front (referred to as prompt  $\text{NO}_x$ ). The quantity of  $\text{NO}_x$  created when a fuel burns depends primarily on temperature, time, and turbulence variables. That is, flame temperature and the residence time of the fuel/air mixture.

along with the nitrogen content of the fuel and the quantity of excess air used for combustion determine the NO<sub>x</sub> levels present in the curing oven atmosphere. By delaying the mixing of fuel and air, low NO<sub>x</sub> burners can reduce combustion temperatures, minimize initial turbulence, and retard the formation of NO<sub>x</sub> in the curing oven to levels of less than 5 parts per million NO<sub>x</sub>.

Once the electrodeposited coating is cured on the substrate as in any of the processes of the present invention, one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions are applied directly to the cured electrodeposited coating.

The use of a primer or primer-surfacer is unnecessary because of the improved photodegradation resistance afforded by the various compositions used in any of the processes of the present invention. Suitable top coats (including base coats, clear coats, pigmented monocoats, and color-plus-clear composite compositions) include any of a variety of top coats known in the art, and each independently may be waterborne, solventborne, in solid particulate form, i.e., a powder coating composition, or in the form of a powder slurry. The top coat typically includes a film-forming polymer, crosslinking material and, if a colored base coat or monocoat, one or more pigments.

Non-limiting examples of suitable base coat compositions include waterborne base coats such as are disclosed in U.S. Patent Nos. 4,403,003; 4,147,679; and 5,071,904. Suitable clear coat compositions include those disclosed in U. S. Patent Nos. 4,650,718; 5,814,410; 5,891,981; and WO 98/14379.

The top coat compositions can be applied by conventional means including brushing, dipping, flow coating, spraying and the like, but they are most often applied by spraying. The usual spray techniques and equipment for air spraying and electrostatic spraying and either manual or automatic methods can be used.

After application of each top coat to the substrate, a film is formed on the surface of the substrate by driving water out of the film by heating or by an air-drying period. Typically, the thickness of a pigmented base coat ranges from about 0.1 to about 5 mils (about 2.54 to about 127 microns), and preferably about 0.4 to about 1.5 mils (about 10.16 to about 38.1 microns). The thickness of a clear coat usually ranges from about 0.5 to about 5 mils (about 12.7 to about 127 microns), preferably about 1.0 to about 3 mils (about 25.4 to about 76.2 microns).

The heating will preferably be only for a short period of time and will be sufficient to ensure that any subsequently applied top coating can be applied without any dissolution occurring at the coating interfaces. Suitable drying conditions will depend on the particular top coat composition and on the ambient humidity (if the top coat composition is waterborne), but in general a drying time of from about 1 to 5 minutes at a temperature of about 80°F to 250°F (20°C to 121°C) is used. Usually between coats, the previously applied coat is flashed, that is, exposed to ambient conditions for about 1 to 20 minutes.

After application of the top coat composition(s), the coated substrate is then heated to a temperature and for a period of time sufficient to effect cure of the coating layer(s). In the curing operation, solvents are driven off and the film-forming materials of the top coats are each crosslinked. The heating or curing operation is usually carried out at a temperature in the range of from 160°F to 350°F (71°C to 177°C) but if needed, lower or higher temperatures may be used as necessary to activate crosslinking mechanisms. Cure is as defined as above.

For purposes of the present invention, the percent light transmission is determined by measuring light transmission of free cured top coat films ranging from 1.9 to 2.2 mils (48.26 to 55.88 micrometers) film thicknesses using a Perkin-Elmer Lambda 9 scanning spectrophotometer with a 150 millimeter Lap Sphere integrating sphere. Data is collected using Perkin-Elmer UV WinLab software in accordance with ASTM E903, Standard Test Method for Solar Absorbance, Reflectance, and Transmittance of Materials Using Integrating Spheres.

In one embodiment, the present invention is directed to a photodegradation resistant multi-layer composite coating comprising a cured primer coating layer over at least a portion of an electroconductive substrate, and a cured top coat layer over at least a portion of the cured primer layer. The primer coating layer is formed from any of the curable electrodepositable coating compositions described in detail above.

The top coat layer can be formed from one or more pigment-containing coating compositions and/or one or more pigment-free coating compositions as described above and is characterized in that the multi-layer composite coating exhibits substantially no interlayer delamination between the cured primer coating layer and the cured top coat layer upon concentrated solar spectral irradiance exposure equivalent to two years outdoor weathering when the top coat layer has at

least 80 percent light transmission as measured at 400 nanometers. Any of the above-described top coating compositions can be used to form the top coat layers of the photodegradation multi-layer composite coating, provided that when cured, the top coat layer has at least 80 percent light transmission as measured at 400  
5 nanometers wavelength. Also, it should be obvious that the improved photodegradation resistance can be observed upon such concentrated solar spectral irradiance only if the cured electrodeposited primer coating has acceptable initial adhesion to the substrate, and the cured multi-layer composite coating exhibits acceptable initial interlayer adhesion. This is because the adhesion failure in such  
10 instances is obviously due to factors other than photodegradation of the cured electrodeposited coating. As used herein, in the specification and in the claims, "concentrated solar irradiance exposure" equivalent to two years outdoor weathering is intended to mean accelerated exposure testing conducted in accordance with SAE J1961 which specifies ASTM G90-98, Standard Practice for Performing Accelerated  
15 Outdoor Weathering of Non metallic Materials Using Concentrated Natural Sunlight, Cycle 3, which utilizes fresnel solar concentrators using the EMMAQUA-NTW<sup>®</sup> (Equatorial Mount with Mirrors for Acceleration, with Water-nighttime wetting) test method, available through ATLAS Weathering Services Group, DSET Laboratories of Phoenix, Arizona. The accelerated exposure testing is conducted for a period of time  
20 and under conditions which correlate to two years outdoor weather exposure (as described in detail below). This method includes the use of a fresnel-reflecting system which employs ten flat first-surface mirrors to concentrate natural sun light onto coated test panel surfaces mounted on a target board. The high quality first-surface mirrors uniformly focus sunlight onto the test panel surfaces at an intensity of  
25 approximately eight times that of global daylight and approximately five times the global radiation in the ultraviolet spectrum. Test panels are sprayed with pure deionized water at pre-determined, regular intervals.

Testing parameters are governed by ISO 877, Plastics - Methods of Exposure to Direct Weathering, to Weathering Using Glass-filtered Daylight, and to Intensified  
30 Weathering by Daylight Using Fresnel Mirrors, and ASTM G90. EMMAQUA exposures are correlated to equivalent "year" of average desert (central Arizona) or subtropical (south Florida) total ultraviolet real-time exposure. (See correlation table below.) For example, see correlation data presented in Bauer, D.R., "Chemical Approaches for Evaluating Automotive Materials and Test Methods," presented at the

Advanced Symposium on Automotive Materials Testing, Scottsdale, AZ, 1993; Bauer, D.R., Paputa Peck, M.C., and Carter, R.O., "Evaluation of Accelerated Weathering Tests for a Polyester-Urethane Coating Using Photoacoustic Infrared Spectroscopy," Journal of Coatings Technology, Dec. 1987, Vol. 59, No. 755, pg. 103-109; Higgins, Dr. Richard J., "Powder Coatings, Focus on Usage Trends," Metal Architecture, Sept. 1991, Vol. 7, No. 9, pg. 56-60 (Figure 2); Keller, D.M., "Testing to Failure of Paint on Plastics," presented at the Advanced Coatings Technology Conference, Chicago, IL, 1992, pg. 133-144; Wineburg, J.P., "Automotive Coatings and Stabilizers," presented at the Advanced Symposium on Automotive Materials Testing, Scottsdale, AZ, 1993; and Zerlaut, G.A. and Robbins, J.S., "Accelerated Outdoor Exposure Testing of Coil Coatings by the EMMAQUA® Test Method," presented at the Advanced Coatings Technology Seminar, Detroit, MI, 1991 (Table 4).

For purposes of the present invention, the concentrated solar spectral irradiance exposure correlates to two years south Florida at 45° outdoor exposure.

As was previously discussed, the transmission of visible and/or ultraviolet radiation through the cured topcoating layer(s) to the cured electrodeposited coating is known to cause photodegradation of the electrodeposited coating at the electrocoating/topcoating interface which can result in interlayer delamination of the topcoat layer from the electrocoat layer. Therefore, to ensure that the topcoat layer(s) have at least 80 percent light transmission measured at 400 nanometers wavelength, two clear (i.e., unpigmented) top coat layers are typically formed over the electrodeposited primer layer. For purposes of testing, the two clear top coat layers are formed from a first or base coat layer which is substantially free of pigment, followed by subsequent application of second or clear coat layer which is also substantially free of pigment.

Metal substrates coated by the processes of the present invention demonstrate excellent corrosion resistance as determined by salt spray and/or other cyclic corrosion resistance testing and excellent resistance to photodegradation. When topcoated with a basecoat and/or clearcoat system having at least 0.1 percent light transmission as measured at 400 nanometers wave length, the resulting multi-layer composite coating exhibits substantially no interlayer delamination or adhesion loss between the cured electrodeposited coating and the subsequently applied top coating layers as determined in accordance with ASTM-3359-97, method B. Further,

the multi-layer composite coating of the present invention exhibits substantially no interlayer delamination or adhesion loss between the cured electrodeposited coating and the subsequently applied top coating layers upon concentrated solar spectral irradiance exposure equivalent to two years outdoor weathering when the top coating layer(s) have at least 80 percent light transmission as measured at 400 nanometers wavelength.

Illustrating the invention are the following examples that are not to be considered as limiting the invention to their details. All parts and percentages in the examples, as well as throughout the specification, are by weight unless otherwise indicated.

#### EXAMPLE A

This example describes the preparation of a cationic amine salt group-containing acrylic resin having a blocked aliphatic polyisocyanate curing agent mixed with the polymer. The resin was used as a component in the electrodepositable coating composition of Example 1 below. The cationic acrylic polymer was prepared as described below from the following ingredients:





1000530-10001  
T090T" 0E8500T

mixture was held for an additional 30 minutes at a temperature ranging between 115°C to 120°C. The reaction mixture then was maintained at a temperature of 120°C during addition of the next three ingredients which were added over a period of 10 to 15 minutes, and the temperature was maintained for 30 minutes. The reaction mixture was cooled to room temperature then diluted with the final charge of methylisobutyl ketone. A sample, which was diluted with Dowanol PM at a ratio of polymer to solvent of 2:1, had a Gardner-Holt bubble viscosity of T-U.

The reaction mixture was heated to 90°C under a nitrogen blanket at which time diethanolamine was added and this mixture was maintained at a temperature of 90°C for one hour. The ketimine was then added followed by and the resultant reaction mixture was maintained at 90°C for an additional one-hour period. The crosslinker was added and the reaction mixture was maintained at 90°C for 20 minutes. A polymer sample was found to have a Gardner-Holt bubble viscosity of R. The last two ingredients were mixed separately and heated to a temperature of 50°C. To this, 94% of the polymer was added under agitation to produce a dispersion of the organic polymer in an aqueous medium having a weight solids of 25 percent. Final distillation to remove methylisobutyl ketone yielded a dispersion having 30.88 percent solids by weight.

#### EXAMPLE B

This example describes the preparation of a cationic amine salt group-containing polyepoxide resin having a blocked aliphatic polyisocyanate curing agent mixed with the polymer. The resin was used as a component in the electrodepositable coating composition of Example 2 below. The cationic polyepoxide resin was prepared as described below from the following ingredients:

INGREDIENTS	PARTS BY WEIGHT
EPON 880 <sup>1</sup>	614.68
Bisphenol A-ethylene oxide adduct <sup>2</sup>	125.00
Bisphenol A	265.42
Methylisobutyl ketone	20.51
Ethyltriphenylphosphonium iodide	0.6
Bisphenol A-ethylene oxide adduct	125.00
Methylisobutyl ketone	21.11
Crosslinker <sup>3</sup>	891.13
Diketimine <sup>4</sup>	57.01
Methylethanolamine	48.68

<sup>1</sup> Diglycidyl ether of bisphenol A having an epoxy equivalent weight of 188, available from Resolution Performance Products.

<sup>2</sup> Reaction product prepared from bisphenol A and ethylene oxide at a molar ratio of 1:6 (100% solids ).

<sup>3</sup> Prepared by reacting 3 equivalents of DESMODUR N 3300 (polyfunctional hexamethylene diisocyanate available from Bayer Corp.) with 3 equivalents of caprolactam, using dibutyltin dilaurate as catalyst (85% solids in methylisobutyl ketone).

<sup>4</sup> Reaction product of diethylenetriamine and methylisobutyl ketone (73% solids in methylisobutyl ketone).

The first four ingredients were added to a suitably equipped reaction vessel and heated under nitrogen atmosphere to a temperature of 125°C.

Ethyltriphenylphosphonium iodide was added and the reaction mixture was allowed to exotherm to a temperature of 145°C. That temperature was maintained for a period of 2 hours at which time the second charge of bisphenol A-ethylene oxide adduct was added and an epoxy equivalent was obtained. The second charge of methylisobutyl ketone, crosslinker, diketimine and methylethanolamine were added sequentially. The resulting reaction mixture was allowed to exotherm and a

temperature of 122°C was established and maintained for a period of one hour. An aqueous dispersion was prepared by adding 1900 parts by weight of the reaction mixture to a mixture of 39.44 parts by weight sulfamic acid and 1255 parts by weight deionized water. To this mixture was added 17.1 parts by weight of a 30% solution of rosin acid in butylcarbitol formal. The dispersion was diluted with 1437 parts by weight deionized water (water added in two stages), then vacuum stripped to remove organic solvent. The resultant product had a solids content of 38.84 percent (1 hour at 110°C).

### EXAMPLE C

This example describes the preparation of a cationic amine salt group-containing polyepoxide resin having a blocked aliphatic polyisocyanate curing agent mixed with the polymer. The resin was used in the electrodepositable coating composition of Example 3 below. The cationic polyepoxide resin was prepared as described below from the following ingredients:

INGREDIENTS	PARTS BY WEIGHT
EPON 880	614.68
Bisphenol A-ethylene oxide adduct of Example B	125.00
Bisphenol A	265.42
Methylisobutyl ketone	20.51
Ethyltriphenylphosphonium iodide	0.6
Bisphenol A-ethylene oxide adduct of Example B	125.00
Methylisobutyl ketone	22.46
Crosslinker of Example B	905.58
Diethanolamine	68.05
Diketimine of Example B	57.01

The first four ingredients were charged to a suitably equipped reaction vessel and heated under a nitrogen atmosphere to a temperature of 125°. Ethyltriphenylphosphonium iodide was then added and the reaction mixture was allowed to exotherm to a temperature of 145°C. The reaction mixture was maintained at that temperature for a period of 2 hours at which time the second charge of bisphenol A-ethylene oxide adduct was added and an epoxy equivalent was obtained. The second charge of methylisobutyl ketone, crosslinker, and diethanolamine then were added sequentially. The resulting reaction mixture was allowed to exotherm and a temperature of 122°C was established. This reaction mixture was maintained at this temperature for a period of 30 minutes at which time the diketimine was added and the resulting reaction mixture was maintained at 122°C for 30 additional minutes. An aqueous dispersion was prepared by adding 1900 parts by weight of the reaction mixture to a mixture of 38.81 parts by weight sulfamic acid and 1255 parts by weight of deionized water. To this mixture was added 17.1 parts by weight of a 30% solution of rosin acid in butylcarbitol formal. The mixture was diluted with 1437 parts by weight deionized water (water added in two stages),

then vacuum stripped to remove organic solvent. The resultant product had a solids content of 37.3 percent (1hour at 110°C).

#### EXAMPLE D

This example describes the preparation of a cationic amine salt group-containing polyepoxide resin having a blocked aliphatic polyisocyanate curing agent mixed with the polymer. The cationic resin is used as a component in the electrodepositable coating composition of Example 4 below. The cationic resin was prepared in two steps as described below.

#### EXAMPLE D-1

This example describes the preparation of a blocked aliphatic polyisocyanate curing agent used in the electrodepositable coating compositions of the present invention. The blocked polyisocyanate was prepared as follows.

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
DESMODUR® N-3300 <sup>1</sup>	1600.0
Methylisobutyl ketone	137.3
Dibutyltin dilaurate	3.0
Caprolactam	340.2
Caprolactam	340.2
Caprolactam	340.2
Methylisobutyl ketone	873.2

<sup>1</sup>A hexamethylene diisocyanate trimer, having an NCO equivalent weight of 194, available from the Bayer Corporation

The first three ingredients were charged to a suitably-equipped vessel under a nitrogen atmosphere. The mixture was heated to 105°C. Upon attaining this temperature, the first portion of caprolactam was added. After an initial exotherm, the reaction mixture was cooled to a temperature of 105°C, at which time the second portion was added. The reaction mixture was then permitted to exotherm, and the temperature was again adjusted to a temperature of 105°C. Upon attaining this temperature, the third portion of caprolactam was added and the reaction mixture was again permitted to exotherm. The temperature then was adjusted to 105°C and the reaction mixture was held at that temperature for 3 hours. The reaction mixture

was monitored by infrared spectroscopy for the disappearance of NCO. Upon disappearance of the NCO peak, the methylisobutyl ketone was added slowly and the reaction mixture was mixed until homogeneous. The final reaction product had a solids content of 69.6 percent (one hour at 110°C).

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#### EXAMPLE D-2

The following example describes the preparation of a cationic amine salt-group-containing polyepoxide resin having the blocked polyisocyanate crosslinker of Example D-1 mixed with the resin. The cationic resin was prepared as follows.

10

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
EPON 880	973.1
Bisphenol A	375.3
MAZON® 1651 <sup>1</sup>	104.7
TETRONIC® 150R1 <sup>2</sup>	0.5
Diethanolamine	56.3
1-Amino-3-N,N-di(2-hydroxyethyl)amino propane <sup>3</sup>	153.8
Crosslinker of Example D-1	2036.5
Deionized water	851.7
Sulfamic acid	28.6
30% Gum rosin solution in MAZON® 1651	13.6
Deionized water	950.6
Deionized water	1600

<sup>1</sup>The formal of 2-(2-butoxyethoxy) ethanol, commercially available from BASF Corporation.

<sup>2</sup>An alkoxyated diamine surfactant, available from BASF Surfactants.

<sup>3</sup>Available from Air Products and Chemicals, Inc.

- 15 The first four ingredients were charged to a suitably equipped vessel, and, under a nitrogen atmosphere, heated to 70°C and held at that temperature for a period of 15 minutes. At that point, the two amines were added. The reaction mixture was permitted to exotherm, after which the temperature was adjusted to 140°C. The reaction mixture was held at that temperature for a period of 2 hours, at which time
- 20 the crosslinker was added, and the reaction mixture was adjusted to a temperature of 120°C. An aqueous dispersion was prepared by dispersing 1600 grams of the resultant reaction mixture in a solution prepared from the eighth and ninth ingredients. The gum rosin solution was added to the dispersion followed by the addition of deionized water. The resulting dispersion was diluted with an additional

quantity of deionized water and heated to a temperature ranging from 60° to 65°C. Organic solvent was removed under reduced pressure to yield an aqueous dispersion having a non-volatile solids content of 26.8% (one hour at 110°C).

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### **EXAMPLE E**

This example describes the preparation of a cationic amine salt group-containing acrylic resin having a blocked aliphatic polyisocyanate curing agent mixed with the polymer. The resin was used as a component in the electrodepositable coating composition of Example 5 below. The cationic acrylic resin was prepared from the following ingredients:

10

<b><u>INGREDIENTS</u></b>	<b><u>PARTS BY WEIGHT</u></b>
DOWANOL PNB	122.5
DOWANOL® PM	157.44
Methylisobutyl ketone	40.02
TINUVIN® 1130	29.58
Ethyl acrylate	661.20
Styrene	121.80
Hydroxypropyl methacrylate	261.00
Methyl methacrylate	487.20
Glycidyl methacrylate	208.80
t-Dodecyl mercaptan	17.40
VAZO-67	43.51
DOWANOL PNB	55.68
DOWANOL PM	27.84
Methylisobutyl ketone	22.27
LUPERSOL-75M	34.80
DOWANOL PNB	27.84
DOWANOL PM	13.92
Methylisobutyl ketone	164.29
Diethanolamine	116.93
Ketimine of Example A	104.40
Crosslinker of Example A	1141.64
Sulfamic acid	112.06
Deionized water	8029.49

The epoxy equivalent weight of the monomer mixture as measured by titration with perchloric acid was found to be 1212, meeting the specification range of 1195-1263. The first four ingredients were charged into a suitably equipped reaction vessel under a nitrogen atmosphere and heated to a temperature of 100°C. The next ten ingredients were added to the vessel over a period of 2.5 hours, and upon completion of the addition, the reaction mixture was maintained at a temperature ranging between 115°C and 120°C for a period of 30 minutes. The reaction mixture was heated to a temperature of 120°C at which time the next three ingredients were added over a period of 10 to 15 minutes, and that temperature was maintained for a period of 30 minutes. The reaction mixture then was cooled to room temperature, and a viscosity sample was drawn. The reaction mixture was then diluted with the final charge of methylisobutyl ketone. The viscosity sample was diluted with DOWANOL PM at a ratio of resin to solvent of 2:1. The sample was found to have a Gardner-Holt bubble viscosity of T-U.

The reaction mixture then was heated to a temperature of 90°C under a nitrogen blanket, at which time diethanolamine was added, and the resulting reaction mixture was maintained for one hour at a temperature of 90°C. The ketimine then was added, and the reaction temperature again maintained at 90°C for one hour. The crosslinker then was added followed by a 20-minute hold period. A viscosity sample was found to have a Gardner-Holt bubble viscosity of Q+. The last two ingredients were separately mixed and heated to a temperature of 52°C, at which time 94% of the reaction mixture prepared as described immediately above was added under agitation to produce a dispersion of the organic resin in an aqueous medium having a solids content of 25 percent (one hour at 110°C). The dispersion was distilled under vacuum to remove organic solvent, yielding a final product having a solids content of 32.23 percent (one hour at 110°C).

#### EXAMPLE F

This example describes the preparation of a cationic amine salt group-containing polyepoxide resin having a blocked aliphatic polyisocyanate curing agent mixed with the polymer. The cationic polyepoxide resin was used as a component in the electrodepositable coating composition of Example 5 below. The cationic polyepoxide resin was prepared from the following ingredients:





### EXAMPLE G

This example describes the preparation of a cationic amine salt group-containing acrylic resin having a blocked aliphatic polyisocyanate curing agent mixed with the polymer. The cationic acrylic resin was used as a component in the electrodepositable coating composition of Example 6 below. The cationic acrylic resin was prepared as described below from the following ingredients:

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Methylpropyl ketone	274.78
TINUVIN® 1130	27.85
Ethyl acrylate	605.23
Styrene	463.25
Hydroxypropyl methacrylate	149.45
Methyl methacrylate	52.30
Glycidyl methacrylate	224.18
t-Dodecyl mercaptan	14.93
VAZO-67	37.34
DOWANOL PNB	47.83
DOWANOL PM	23.90
Methylisobutyl ketone	19.38
LUPERSOI-75M	29.95
DOWANOL PNB	23.90
Methylisobutyl ketone	11.95
Diethanolamine	134.16
Ketimine of Example A	109.68
Crosslinker <sup>†</sup>	1973.42
Sulfamic acid	89.45
Deionized water	9033.12

<sup>†</sup> Blocked polyisocyanate curing agent prepared by reacting 10 equivalents of isophorone diisocyanate with 1 equivalent of trimethylol propane, 3 equivalents of bisphenol A-ethylene oxide polyol (prepared at a bisphenol A to ethylene oxide molar ratio of 1:6 (100% solids), and 6 equivalents of primary hydroxyl from butylene glycol.

The first two ingredients were charged into a suitably equipped reaction vessel under a nitrogen atmosphere and heated to a temperature of 101°C. The next ten ingredients were added to the reaction vessel over a period of 2.5 hours. When the addition was complete, the reaction mixture was maintained at a temperature ranging between 103°C and 108°C for a period of 30 minutes. The reaction mixture

then was heated to a temperature of 120°C at which time the next three ingredients were added over a period of 10 to 15 minutes and maintained at a temperature of 120°C for a period of 30 minutes. The reaction mixture then was cooled to room temperature and viscosity sample was drawn. The sample was diluted with  
5 DOWANOL PM at a resin to solvent ratio of 2:1 and was found to have a Gardner-Holt bubble viscosity of K-L. The reaction mixture then was heated to a temperature of 110°C under a nitrogen blanket, at which time diethanolamine was added, and the reaction mixture was maintained at a temperature of 110°C for a period of one hour. The ketimine then was added followed by another one-hour hold period, and the  
10 crosslinker then was added followed by an additional 20-minute hold period. A viscosity sample then was drawn and measured to have a Gardner-Holt bubble viscosity of T-U. The last two ingredients were mixed separately and heated to a temperature of 50°C. An aqueous dispersion was prepared by adding under agitation 95% of the resin prepared as described immediately above. This dispersion  
15 had a solids content of 25 percent by weight. Organic solvent was removed by distillation to yield a final product having a solids content of 28.6 percent by weight (one hour at 110°C).

#### EXAMPLE H

20 This example describes the preparation of a cationic amine salt group-containing polyepoxide resin having a blocked aliphatic polyisocyanate curing agent mixed with the polymer. The cationic polyepoxide resin was used as a component in the electrodepositable coating composition of Example 6 below. The cationic polyepoxide resin was prepared from the following ingredients:

INGREDIENTS	PARTS BY WEIGHT
Epon 880	448.71
Bisphenol A-ethylene oxide ratio) of Example B	91.25
Bisphenol A	193.76
Methylisobutyl ketone	6.95
Ethyltriphenylphosphonium iodide	0.44
Bisphenol A-ethylene oxide adduct of Example B	91.25
Methylisobutyl ketone	4.55
Crosslinker <sup>1</sup>	833.59
Methylisobutyl ketone	18.33
Diethanolamine	42.99
Diketimine of Example B	65.71
Epon 880 (85% solution in methylisobutyl ketone)	18.96
TINUVIN®123 <sup>2</sup>	16.12

- <sup>1</sup> Blocked polyisocyanate curing agent prepared by adding 10 equivalents of DESMODUR N 3300 (a polyfunctional aliphatic isocyanate resin based on hexamethylene diisocyanate available from Bayer Corp.) to a mixture of 5 equivalents of 1,2-butanediol and 5 equivalents of benzyl alcohol, using dibutyl tin dilaurate as a catalyst ( 87% solids in methylisobutyl ketone).

<sup>2</sup> A hindered amine light stabilizer, available from Ciba-Geigy Corp.

- The first four ingredients were charged to a suitably equipped reaction vessel and heated under a nitrogen atmosphere to a temperature of 125°C. Ethyl triphenylphosphonium iodide then was added and the reaction mixture was allowed to exotherm to a temperature of 145°C. The reaction mixture was held at that temperature for a period of 2 hours, at which time the second charge of bisphenol A-ethylene oxide adduct was added and an epoxy equivalent was obtained. The second charge of methylisobutyl ketone, crosslinker, methylisobutyl ketone, and diethanolamine then were added sequentially. The reaction mixture was allowed to exotherm and a temperature of 122°C was established. The reaction mixture was maintained at that temperature for a period of 30 minutes at which time the diketimine was added, and the reaction temperature was maintained at 122°C for an additional one hour period. To this reaction mixture was added EPON 880 (85% solution in methylisobutyl ketone) and the reaction mixture was held at 122°C for 30 minutes. TINUVIN 123 then was added and the temperature was maintained at 122°C for 30 minutes. An aqueous dispersion was prepared by adding 1500 parts by weight of the reaction mixture prepared as described immediately above to a mixture

of 29.71 parts of sulfamic acid and 971 parts of deionized water. The dispersion was diluted with 1119 parts by weight of deionized water (added in two stages) and the resulting dispersion was vacuum stripped to remove organic solvent. The final product had content of 39.58 percent (one hour at 110°).

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EXAMPLE I

This example describes the preparation of a cationic polyepoxide resin having the blocked aliphatic crosslinker mixed with the polyepoxide polymer. The polyepoxide resin was used as a component in the electrodepositable coating compositions of Example 7 below. The cationic polyepoxide resin was prepared as described below from the following ingredients:

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
EPON 880	89.7
Co-resin <sup>1</sup>	18.3
Bisphenol-A	38.7
Methyl isobutyl ketone	1.4
Ethyltriphenyl phosphonium iodide	0.088
Co-resin <sup>1</sup>	18.3
Methyl isobutyl ketone	2
Crosslinker <sup>2</sup>	139
Methyl isobutyl ketone	4.5
Diethanolamine	10
Diketimine <sup>3</sup>	8.3
EPON 880 (85% solution in MIBK)	3.48
TINUVIN 123	2.95

<sup>1</sup> Bisphenol A-ethylene oxide adduct (1/6 molar ratio) available from BASF Corporation.

<sup>2</sup> Prepared by adding 10 equivalents of a polyfunctional aliphatic isocyanate resin based on hexamethylene diisocyanate (DESMODUR N 3300, available from Bayer corporation) to a mixture of 5 equivalents of 1,2-butanediol and 5 equivalents of benzyl alcohol using dibutyl tin dilaurate as a catalyst. The crosslinker is 87% solids in methyl isobutyl ketone.

<sup>3</sup> Derived from diethylenetriamine and methyl isobutyl ketone (73% solids in methyl isobutyl ketone).

The EPON 828, initial charge of bisphenol A-ethylene oxide adduct, bisphenol A, and the initial charge of methyl isobutyl ketone were charged into a suitably equipped reaction vessel and heated under a nitrogen atmosphere to a temperature of 125°C. Ethyl triphenyl phosphonium iodide then was added and the reaction mixture allowed to exotherm to a temperature of about 145°C. The reaction was held

at 145°C for 2 hours, the second charge of bisphenol A-ethylene oxide adduct was added, and an epoxy equivalent was obtained. The second charge of methyl isobutyl ketone, crosslinker, methyl isobutyl ketone and diethanolamine were added sequentially. The mixture was allowed to exotherm and then a temperature of 122°C was established. The reaction mixture was maintained at a temperature of 122°C for 30 minutes and the diketimine was added. This reaction mixture was maintained at a temperature of 122°C for one hour, at which time EPON 880 in methyl isobutyl ketone was added and the mixture was held for 30 minutes at 122°C. TINUVIN 123 then was added and the temperature was maintained at 122°C for 30 minutes. The reaction mixture (330 parts) was dispersed in aqueous medium by adding it to a mixture of 9.2 parts of sulfamic acid and 225.7 parts of deionized water. To this was added 4.7 parts of surfactant (a 50/50 mixture of SURFYNOL 104 and the N-hydroxyethyl imidazoline of coconut fatty acid neutralized to 75% total theoretical neutralization with acetic acid) available from Air Products and Chemicals, Inc., and 2.95 parts of a 30% solution of rosin acid in butylcarbitol formal. The dispersion was further diluted with 117.8 parts of deionized water and 127.1 parts of deionized water in separate additions. The resultant dispersion was vacuum stripped to remove organic solvent yielding a dispersion having a solids content of 40.62 percent.

#### EXAMPLE J

This example describes the preparation of a cationic acrylic resin used in the electrodepositable coating composition of Example 7 below. The acrylic resin was prepared as described below from the following ingredients:

<b><u>INGREDIENTS</u></b>	<b><u>PARTS BY WEIGHT</u></b>
Methyl propyl ketone	274.78
TINUVIN® 1130	27.85
Ethyl acrylate	605.23
Styrene	463.25
Hydroxypropyl methacrylate	149.45
Methyl methacrylate	52.3
Glycidyl methacrylate	224.18
t-Dodecyl mercaptan	14.93
VAZO-67	37.34
PROPASOL B	47.83
DOWANOL PM	23.9
Methyl isobutyl ketone	19.38
LUPERSOL-75M	29.95
PROPASOL B	23.9
Methyl isobutyl ketone	4.78
Diethanolamine	134.16
Ketimine of Example I	109.68
Crosslinker <sup>1</sup>	1255.88
Sulfamic acid	88.51
Deionized Water	7771.22

<sup>1</sup>Crosslinker is prepared by reacting one equivalent of isocyanurated hexamethylene diisocyanate with one mole of dibutylamine according to a procedure described in US 4,576,979.

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The first two ingredients were charged into a suitable equipped reaction vessel under a nitrogen atmosphere and heated to a temperature of 100°C. The next ten ingredients were fed into the vessel over a period of 2.5 hours. When the feed was complete, the reaction mixture was maintained for an additional 30 minutes at a temperature between 115°C and 120°C. At the end of the hold period, the reaction vessel was heated to 120°C and the next three ingredients were added over a period of 10 to 15 minutes, followed by a 30-minute hold period. The reaction mixture was cooled to room temperature then sampled for bubble viscosity measurement. The sample was diluted with Dowanol PM at a 2:1 resin:Dowanol PM had a viscosity of K.

10 The next day, the reaction mixture was heated to 110°C under a nitrogen blanket. To this, diethanolamine was added followed by a one hour hold at 110°C. The

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diketimine was then added followed by another one hour hold. Finally, the crosslinker was added followed by a 20- minute hold. A sample was taken after the hold for viscosity measurement and the sample was found to have a Gardner-Holt bubble viscosity of Z. The last two ingredients were mixed and heated to 52°C then 94% of the resin was added under agitation to produce a dispersion of the organic resin in an aqueous medium at 25% solids by weight. Final distillation to remove methyl isobutyl ketone gave a dispersion at 23.9% solids (one hour at 110°C).

# ELECTRODEPOSITABLE COATING COMPOSITIONS:

## EXAMPLE 1

This example describes the preparation of an electrodepositable coating composition of the present invention based on the cationic acrylic resin of Example A. The coating composition was prepared from a mixture of the following ingredients:

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Cationic resin of Example A	2283.5
Pigment paste <sup>1</sup>	170.1
Catalyst paste <sup>2</sup>	22.0
Deionized water	1324.4

<sup>1</sup> The pigment paste was prepared by sequentially adding the ingredients listed below under high shear agitation. When the ingredients were thoroughly blended, the paste was transferred to a vertical sand mill and ground to a Hegman value of about 7.25.

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Cationic grind resin <sup>a</sup>	3268.0
Ti-Pure R-900 <sup>b</sup>	5940.0
CSX-333 <sup>c</sup>	60.0
Deionized water	732.0

<sup>a</sup> Prepared as described in U.S. Patent No., 4,715,898, Example 4, except that the ethylene glycol monobutyl ether was replaced with a mixture of propylene glycol butyl ether and propylene glycol methyl ether (solids content of 31%).

<sup>b</sup> Titanium dioxide pigment available from E. I. DuPont de Nemours & Co.

<sup>c</sup> Carbon black beads available from Cabot Corp.

<sup>2</sup> The catalyst paste was prepared by sequentially adding the ingredients listed below under high shear agitation. When the ingredients were thoroughly blended, the paste was transferred to a vertical sand mill and ground to a Hegman value of about 7.25.

<b><u>INGREDIENTS</u></b>	<b><u>PARTS BY WEIGHT</u></b>
Cationic grind resin <sup>a</sup>	527.7
n-butoxypropanol	6.9
FASCAT 4201 <sup>b</sup>	312.0
Deionized water	59.8

<sup>a</sup> Prepared as described in U.S. Patent No. 4,715,898, Example 4, except that the ethylene glycol monobutyl ether was replaced with a mixture of butylcarbitol formal and propylene glycol butyl ether, and 2% by weight ICOMREEN T surfactant was added (solids content of 31%).

<sup>b</sup> Dibutyltin oxide catalyst, commercially available from Atofina Chemicals.

The electrodepositable coating composition in the form of an electrodeposition bath was prepared by adding 300 parts of the deionized water to the cationic resin under agitation. The pigment paste and catalyst paste were separately mixed under agitation and diluted with 300 parts of the deionized water. The paste admixture then was blended with the diluted resin under agitation. The remainder of the deionized water was then added under agitation. Final bath solids were 22 weight percent, with a pigment to resin ratio of 0.15:1.0. The bath was mixed under mild agitation for about two hours. Twenty percent of the total paint weight was removed by ultrafiltration and replaced with deionized water.

## EXAMPLE 2

20 This example describes the preparation of an electrodepositable coating composition of the present invention based on the cationic polyepoxide resin of Example B. The coating composition was prepared from a mixture of the following ingredients:

<b><u>INGREDIENTS</u></b>	<b><u>PARTS BY WEIGHT</u></b>
Cationic resin of Example B	1395.2
Co-resin <sup>1</sup>	98.7
Pigment paste <sup>2</sup>	140.8
Catalyst paste <sup>3</sup>	18.0
Deionized water	2147.3

Prepared as follows: 639.65 g of DER 732 (diglycidyl ether of polypropylene glycol available from Dow Chemical Co.) and 156.27 g of bisphenol A were charged to a suitable reaction vessel and heated to 130°C until the epoxy equivalent weight of the reaction mixture was 1230. The reaction mixture was then cooled to 100°C at which time 71.63 g MAZON 1652 (butyl diethylene glycol formal available from BASF Corp.) was added followed by the addition of 164.92 g of JEFFAMINE D400 (liquid epoxy resin available from Resolution Performance Products). The mixture was held at 90° to 95°C for 4 hours at which time a



sample diluted with methoxy propanol (10g resin and 8.7 g methoxy propanol) had a Gardner-Holt bubble viscosity of K. A mixture of 19 g EPON 828 AND 3.07 g of MAZON 1651 was then added and the mixture was maintained at a temperature of 90° to 95°C for 80 minutes at which time a sample diluted with methoxy propanol (10g resin and 8.7g methoxy propanol) had a Gardner-Holt bubble viscosity of P-Q. Of this mixture, 896.26 g was poured into a solution of 34.83 g sulfamic acid and 1065.19 g deionized water and 58.20 g MONAZOLINE T (a N-hydroxyethyl imidazoline of tall oil fatty acid available from Mona Industries, Inc.) with agitation to form a viscous aqueous dispersion. After mixing for 30 minutes, 586.99 g deionized water were added under agitation. The final aqueous dispersion had a measured solids content of 35% (one hour at 110°C).

<sup>2</sup> The pigment paste was prepared by sequentially adding the ingredients listed below under high shear agitation. When the ingredients were thoroughly blended, the paste was transferred to a vertical sand mill and ground to a Hegman value of about 7.25.

INGREDIENTS	PARTS BY WEIGHT
Cationic grind resin <sup>a</sup>	2158.3
Ti-Pure R-900	3564.0
CSX-333	36.0
Deionized water	241.7

<sup>a</sup> Prepared as described in Example F of U.S. Patent No. 5,130,004, except that ethylene glycol monobutyl ether was replaced with a mixture of propylene glycol butyl ether and propylene glycol methyl ether (solids content 31%).

<sup>3</sup> The catalyst paste was prepared by sequentially adding the ingredients listed below under high shear agitation. When the ingredients were thoroughly blended, the paste was transferred to a vertical sand mill and ground to a Hegman value of about 7.25.

INGREDIENTS	PARTS BY WEIGHT
Cationic grind resin <sup>a</sup>	527.7
n-butoxypropanol	6.9
Dibutyltin oxide	312.0
Deionized water	59.8

<sup>a</sup> Prepared as described in Example 4 of U.S. Patent No. 4,715,898 except that the ethylene glycol monobutyl ether was replaced with a mixture of butylcarbitol formal and propylene glycol butyl ether, and with the addition of 2% by weight on solids of ICOMEEN T, a surfactant available from BASF Corp.

The electrodepositable coating composition in the form of an electrodeposition bath was prepared by first diluting the co-resin with 300 parts of the deionized water under agitation. The cationic resin was then added under agitation. The pigment paste and catalyst paste were separately mixed under agitation and diluted with 300 parts of the deionized water. The paste admixture then was blended with the diluted resin admixture under agitation. The remainder of the deionized water was then added under agitation. Final bath solids were eighteen weight percent, with a pigment to resin ratio of 0.15:1.0.

The bath was mixed under mild agitation for about two hours. Thirty percent of the total paint weight was removed by ultrafiltration and replaced with deionized water.

### EXAMPLE 3

This example describes the preparation of an electrodepositable coating composition of the present invention based on the cationic polyepoxide resin of Example C. The coating composition was prepared from a mixture of the following ingredients:

INGREDIENTS	PARTS BY WEIGHT
Cationic resin of Example C	1451.3
Co-resin <sup>1</sup>	115.2
Pigment paste of Example 2	140.8
Catalyst paste of Example 2	18.0
Deionized water	2074.7

<sup>1</sup> Prepared as follows: 639.65 g of DER 732, 156.27 g of bisphenol A, and 10.97 g ethylene glycol monobutyl ether were charged to a suitable reaction vessel and heated to a temperature of 103°C. 1.5 g of benzyldimethylamine were then added and the reaction mixture was held at 135°C until the epoxy equivalent weight of the reaction mixture was 1250, at which time 52.7 g of ethyleneglycol monobutyl ether were added and the reaction mixture was cooled to 100°, at which time 164.92 g JEFFAMINE D400 were added. The mixture was held at 95°C for a period of 4 hours at which time a sample diluted with methoxy propanol (10g resin and 8.7 g methoxy propanol) had a Gardner-Holt bubble viscosity of K. A mixture of 19.38 g EPON 828 and 3.07 g of ethylene glycol monobutyl ether were then added and the mixture was held at 95°C for 80 minutes at which time a sample diluted with methoxy propanol (10 g resin and 8.7 g solvent) had a Gardner-Holt bubble viscosity of P-Q. Of this reaction mixture, 889.49 g were then poured into a mixture of 29.07 lactic acid (88% solution) and 929.18 g deionized water with agitation to form a viscous aqueous dispersion. After mixing for 30 minutes, 1009.15 g deionized water were added under agitation. The final aqueous dispersion had a measured solids content of 30% (one hour at 110°).

The electrodepositable coating composition in the form of an electrodeposition bath was prepared by first diluting the co-resin with 300 parts of the deionized water under agitation. The cationic resin was then added under agitation. The pigment paste and catalyst paste were separately mixed under agitation and diluted with 300 parts of the deionized water. The paste admixture then was blended with the diluted resin admixture under agitation. The remainder of the deionized water was then added under agitation. Final bath solids were eighteen weight percent, with a pigment to resin ratio of 0.15:1.0. The bath was mixed under mild agitation for about two hours. Thirty percent of the total paint weight was removed by ultrafiltration and replaced with deionized water.

#### EXAMPLE 4

This example describes the preparation of an electrodepositable coating composition of the present invention based on the cationic polyepoxide resin of Example D. The coating composition was prepared from a mixture of the following ingredients:

INGREDIENTS	PARTS BY WEIGHT
Cationic resin of Example D	2251.83
Co-resin <sup>1</sup>	132.18
Pigment paste of Example 2	154.17
Catalyst paste <sup>2</sup>	21.31
Deionized water	1240.51
Diethylene glycol Hexyl ether	45.00

<sup>1</sup> Prepared from the reaction product of 639.65 g of DER. 732 (a diglycidyl ether of polypropylene glycol available from Dow Chemical Co.), 156.27 g of bisphenol A, and 10.97 g of ethylene glycol monobutyl ether were charged to a suitably equipped reaction vessel and heated to a temperature of 130°C. 1.5 g of benzyldimethyl amine was then added and the reaction mixture was held at a temperature of 135°C until the epoxy equivalent weight of the reaction mixture was 1250. 52.7 g of ethylene glycol monobutyl was added and the reaction mixture was then cooled to a temperature of 100°C, at which time 164.92 g of JEFFAMINE D400 (a polyoxypropylene diamine available from Huntsman Corp.) was then added. The reaction mixture was held at a temperature of 95°C for 4 hours at which time a sample diluted with methoxy propanol (10g resin and 8.7 g methoxy propanol) had a Gardner-Holt viscosity of "K". A mixture of 19.38 g EPON 828 (a liquid epoxy resin available from Resolution Performance Products) and 3.07g of ethylene glycol monobutyl ether was then added and the mixture was held at 95°C for 80 minutes at which time a sample diluted with methoxy propanol (10g resin + 8.7 g methoxy propanol) had a Gardner-Holt viscosity of "P-Q". 889.49g of the reaction mixture was then poured into a mixture of 17.05g acetic acid and 941.2g deionized water with agitation to form a viscous aqueous dispersion. After mixing for 30 minutes, 923.87g deionized water was added and mixed until well blended. The final aqueous dispersion had a solids content of 30% (one hour at 110°C).

<sup>2</sup> Prepared by sequentially adding the ingredients listed below under high shear agitation. When the ingredients were thoroughly blended, the paste was transferred to a vertical sand mill and ground to a Hegman value of about 7.25.

INGREDIENTS	Parts by Weight
Cationic grind resin <sup>a</sup>	208.07
Deionized water	269.63
Dibutyltin Oxide	293.18
Deionized water	171.28

<sup>a</sup> Prepared as described in U.S. Patent No. 4,007,154, Example II.

The electrodepositable coating composition, in the form of an electrodeposition bath was prepared by adding each of the above ingredients sequentially under agitation. The resulting electrodeposition bath had a solids content of 20 percent based on total weight of the bath, a pH of 5.54, and a conductivity of

1395 micro-Siemans as measured using an ACCUMET pH/conductivity meter, available from Fisher Scientific, Inc.

#### EXAMPLE 5

5            This example describes the preparation of three electrodepositable coating compositions of the present invention comprising the cationic acrylic resin of Example E and the cationic polyepoxide resin of Example F. Comparative Example 5A describes the preparation an electrodeposition bath containing no soluble iron, Example 5B describes the preparation of an electrodeposition bath containing 15 parts per million of soluble iron, and Example 5C describes the preparation of an electrodeposition bath containing 30 parts per million of soluble iron. Each of the electrodepositable compositions were prepared as described below from a mixture of the following ingredients.

<u>INGREDIENTS</u>	<u>EXAMPLE 5A*</u> (Parts by Weight)	<u>EXAMPLE 5B</u> (Parts by Weight)	<u>EXAMPLE 5C</u> (Parts by Weight)
Cationic resin of Example E	1314.8	1314.8	1314.8
Cationic resin of Example F	580.5	580.5	580.5
Co-resin of Example 2	47.6	47.6	47.6
Pigment paste of Example 1	170.1	170.1	170.1
Catalyst paste of Example 1	22.0	22.0	22.0
Deionized water	1665.0	1665.0	1665.0
Iron (II) acetate <sup>4</sup>	---	0.187	0.374

\* Comparative example.

15            Each of the above electrodepositable coating compositions was prepared in the form of an electrodeposition bath as follows. The cationic resin of Example F and the co-resin were blended under agitation as 300 parts of deionized water were slowly added to the admixture. The admixture was then added to the Cationic resin of Example E. The pigment paste and the catalyst paste were mixed separately and diluted with 300 parts of deionized water, then blended with the resin admixture. The remainder of the deionized water was then added to this admixture under agitation. The composition was mixed under mild agitation for about two hours. Final bath solids were about 22 percent by weight, with a pigment to resin ratio of 0.15:1.0.

20            Twenty percent of the total bath weight was removed by ultrafiltration and replaced

with deionized water. Iron (II) acetate was added under agitation to the compositions of Examples 5B and 5C.

#### EXAMPLE 6

This example describes the preparation of an electrodepositable coating composition of the present invention based on the cationic acrylic resin of Example G and the cationic polyepoxide resin of Example H. The coating composition was prepared from a mixture of the following ingredients:

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Cationic resin of Example G	1447.7
Cationic resin of Example H	697.3
E6251 <sup>†</sup>	237.5
Catalyst paste of Example 1	6.6
Deionized water	1410.9

<sup>†</sup> Pigment paste commercially available from PPG Industries, Inc.

The electrodepositable coating composition was prepared in the form of an electrodeposition bath as follows. To the cationic resin of Example G was added 300 parts of deionized water under agitation, then the cationic resin of Example H is added. The pigment paste and the catalyst paste were separately mixed under agitation and diluted with 300 parts of deionized water. The paste admixture then was added under agitation to the resin admixture, followed by addition of the remainder of the deionized water. The composition was blended under mild agitation for about two hours. Final bath solids were about 22 percent, with a pigment to resin ratio of 0.15:1.0. Twenty percent of the total bath weight was removed by ultrafiltration and replaced with deionized water.

#### TEST PANEL PREPARATION:

Each of the electrodepositable coating compositions of Examples 1 through 5, and a comparative conventional electrodepositable composition, prepared as described in U.S. Patent No. 5,389,219, Example 2, was electrodeposited onto 4" X 12" zinc-phosphated galvanized steel test panels commercially available from ACT Laboratories, Inc. as APR23834(B) (E60 EZG 60G, two-sided with C700 C18 phosphate and rinse). Each of the compositions was electrodeposited on the aforementioned substrates under conditions necessary to form a substantially continuous film having a film thickness of approximately 1 mil (25.4 micrometers) on

the substrate. The electrocoated test panels were thermally cured as follows: one set was cured at 360°C for 30 minutes in an electric oven; one set was cured at 395°C for 60 minutes in an electric oven; and one set was cured at 395°C for 60 minutes in a gas-fired oven.

- 5           The test panels were then top coated with a solvent-based unpigmented base/clear top coat system which was designed to permit 80 percent light transmission measured at 400 nanometers wavelength. The base coat composition is as follows:

<b>INGREDIENTS</b>	<b>Parts by Weight</b>
Methyl ethyl ketone	94.1
Xylene	280.4
Diisobutyl ketone	490.7
Amyl alcohol	80.7
TINUVIN 328 <sup>1</sup>	60.5
Microgel <sup>2</sup>	458.1
RESIMENE 755 <sup>3</sup>	1008.3
Polyester resin <sup>4</sup>	100.8
Acrylic resin <sup>5</sup>	1038.1
Methanol	121.1
Catalyst <sup>6</sup>	67.2

<sup>1</sup> Ultraviolet light absorber available from Ciba Specialty Chemicals.

<sup>2</sup> Prepared as described in U.S. Paten No. 4,147,688, Example II.

<sup>3</sup> Melamine-formaldehyde crosslinker available from Solutia, Inc.

<sup>4</sup> Condensation reaction product of a C<sub>36</sub> dibasic acid (59.1% of reactant solids) and neopentyl glycol (16.9% of reactant solids), cyclohexane dimethanol (17.5% of reactant solids), and trimethylol propane (6.5% of reactant solids)(100% total solids).

<sup>5</sup> Hydroxy functional acrylic resin (18.5% n-butyl methacrylate/40 hydroxypropyl acrylate/0.5% methyl methacrylate/20% styrene/19% n-butyl acrylate/2% acrylic acid), 68.8% solids in a mixture of acetone, Aromatic 100 and amyl acetate.

<sup>6</sup> Diisopropylamine neutralized dodecylbenzene sulfonic acid.

20           The base coat composition was spray applied to each of the electrocoated test panels to yield a base coat dry film thickness of about 0.35 mils (8.89 micrometers). The applied base coat was given a one minute flash period. A solvent-based clear coat, DCT 1002B (available from PPG Industries, Inc.) then was  
25   spray-applied to the base coat to give a dry clear coat film thickness of 1.6 to 1.8 mils (40.64 to 15.72 micrometers). The test panels were then thermally cured at a temperature of 250°F (121.1°C) for 30 minutes.

Light transmission of the base coat/clear coat system was determined using cured free films applied at the dry film thickness described above using a Perkin-Elmer Lambda 9 scanning spectrophotometer with a 150 millimeter Lab Sphere integrating sphere. Data collection was accomplished with Perkin-Elmer UV WinLab software in accordance with ASTM E903.

Photodegradation resistance was evaluated as described above in accordance with ASTM G90-98 using EMMAQUA NTW®, available through Atlas Weather Services, Inc., DSET Laboratories of Phoenix, Arizona. The test panels were cooled by forced air convection to limit the increase in surface temperatures of the specimens to 10°C above the maximum surface temperature when identically mounted specimens are exposed to direct sunlight at normal incidence at the same time and location without concentration. Exposure is reported as the total integrated UV radiation ranging between wavelengths of 295 and 385 nanometers.

Two panels sets from each of the three curing schemes discussed above (2" X 5.5" panels) were tested using the above method. For one panel set ("set 1"), half of each panel was masked with aluminum foil at an exposure of 145 MJ/m<sup>2</sup>. The test panels of set 1 were removed from exposure and evaluated for photodelamination resistance after an exposure of 290 MJ/m<sup>2</sup>. Half of each panel of the second set ("set 2") was masked with aluminum foil at an exposure of 435 MJ/m<sup>2</sup>. Set 2 was removed from exposure for evaluation after an exposure of 580 MJ/m<sup>2</sup>. Total integrated UV radiation ranged between wavelengths of 295 and 385 nanometers.

As previously discussed, the weathering exposure testing done in accordance with this method has been correlated with south Florida exposure at 45° south. Exposure correlation is as follows:

Exposure Energies (MJ/m <sup>2</sup> )	Equivalent Florida Exposure (40° South)
145	6 months
290	12 months
435	18 months
5880	24 months

Photodegradation resistance of the cured electrodeposited coating was evaluated by crosshatch adhesion testing of the exposed test panels at each of the

aforementioned exposure energies. Adhesion testing was conducted after each of the test panels had been exposed for 16 hours at 100% relative humidity at 100°F. Cross-hatch adhesion testing was done in accordance with ASTM D3359-97, using a rating scale ranging from 0 to 10, where 10 + best, and using a 2 millimeter

- 5 crosshatch tool (Model PA-2056, available from BYK Gardner).

Adhesion results are reported below in Tables 1 and 2 below.



TABLE 1

ADHESION TEST RESULTS

Example #	Cure Conditions	Initial Adhesion	Post Humidity	145 NJ/m <sup>2</sup> Adhesion	290 NJ/m <sup>2</sup> Adhesion	Post Humidity	435 NJ/m <sup>2</sup> Adhesion	Post Humidity	580 NJ/m <sup>2</sup> Adhesion	Post Humidity
1	30' @ 350°F E	8 TI	9 TI	8 TI	9 TI	9 TM	9 TM B	7 TM	10	5 TM
	60' @ 385°F E	6 TI	4 TI	9 TI	9 TI	6 TM	10	8 TI	9 TI	6 TM
	60' @ 385°F G	8 TI	6 TI	10	10	8 TI	9 TI B	8 TI	10	8 TM
2	30' @ 360°F E	10	10	10	10	10	10 B	10	10	10
	60' @ 395°F E	10	10	10	10	10	10 B	10	10	10
	60' @ 395°F G	10	10	10	10	0 TI	3 B TI	3 TI	4 TI	0 TI
3	30' @ 360°F E	10	10	10	10	10	10 B	10	10	10
	60' @ 395°F E	10	10	10	10	10	10 B	10	10	10
	60' @ 395°F G	10	10	10	10	0 TI	0 TI	0 TI	5 TI	0 TI
4	30' @ 360°F E	10	10	10	10	10	9 B TI	5 TI	8 TI	0 TI
	60' @ 395°F E	10	10	10	10	10	6 TI B	4 TI	6 TI	0 TI
	60' @ 395°F G	10	10	1 TI	0 TI	0 TI	0 TI B	0 TI	1 TI	0 TI
ED5070 <sup>1</sup>	30' @ 340°F E	9	9	10	0 TI	0 TI	2 TI	0 TI	0 TI	0 TI
(Comparative)	60' @ 375°F E	9	9	10	0 TI	0 TI	1 TI	0 TI	0 TI	0 TI
	60' @ 375°F G	10	10	0 TI	0 TI	0 TI	0 TI	0 TI	0 TI	0 TI

<sup>1</sup> Cationic electrodeposition primer available from PPG Industries, Inc.

Failure, is considered to be a rating of less than 7 with a failure mode of TI.

Codes: B = Blushing of Clear Coat

TI = Intercoat failure at Electrocoat/Basecoat interface

TM = Adhesion failure at the Electrocoat/Metal interface

G = Gas Oven

E = Electric Oven

TABLE 2

ADHESION TEST RESULTS

Example #	Cure Conditions	Initial Adhesion	Post Humidity	145 NJ/m <sup>2</sup> Adhesion	Post Humidity	290 NJ/m <sup>2</sup> Adhesion	Post Humidity	435 NJ/m <sup>2</sup> Adhesion	Post Humidity	580 NJ/m <sup>2</sup> Adhesion	Post Humidity
5A*	30' @ 350°F E	10	10	10	10	10	10	9.5 B	10	10	10
	60' @ 385°F E	10	10	10	10	10	10	9 B	10	10	10
	60' @ 385°F G	10	10	10	10	10	10	10 B	10	10	10
5B	30' @ 350°F E	10	10	10	10	10	10	10 B	10	10	10
	60' @ 385°F E	10	10	10	10	10	10	10 B	10	10	8 TM
	60' @ 385°F G	10	8 TI	10	10	10	10	9 B	10	10	9
5C	30' @ 350°F E	10	10	10	10	10	10	9 B	10	10	10
	60' @ 385°F E	10	9 TI	10	10	10	10	10	10	10	10
	60' @ 385°F G	9 TI	8 TI	10	10	10	10	8 B TI	5 TI	9 TI	6 TI

\* Comparative Example.

Codes: B = Blushing of Clear Coat

TI = Intercoat failure at Electrocoat/Basecoat interface

TM = Adhesion failure at the Electrocoat/Metal interface

G = Gas Oven

E = Electric Oven

### EXAMPLE K

This example describes the preparation of a cationic polyepoxide resin having a blocked polyisocyanate curing agent mixed with the polymer. The cationic resin was used as a component in the electrodepositable composition of Example 7 below.

- 5 The cationic polyepoxide resin was prepared as described below from the following ingredients:

INGREDIENTS	PARTS BY WEIGHT
EPON 880	89.7
Co-resin <sup>1</sup>	18.3
Bisphenol-A	38.7
Methyl isobutyl ketone	1.4
Ethyltriphenyl phosphonium iodide	0.088
Co-resin <sup>1</sup>	18.3
Methyl isobutyl ketone	2
Crosslinker of Example 1	139
Methyl isobutyl ketone	4.5
Diethanolamine	10
Diketimine <sup>2</sup>	8.3
EPON 880 (85% solution in MIBK)	3.48
TINUVIN 123	2.95

<sup>1</sup> Bisphenol A-ethylene oxide adduct (1/6 molar ratio).

<sup>2</sup> Diketimine is derived from diethylenetriamine and methyl isobutyl ketone (73% solids in methyl isobutyl ketone).

The EPON 828, initial charge of the co-resin, bisphenol A and the initial charge of methyl isobutyl ketone were charged to a suitably equipped reaction vessel and heated under a nitrogen atmosphere to a temperature of 125°C. Ethyl triphenyl phosphonium iodide then was added and the reaction mixture allowed to exotherm to about 145°C. The reaction was held at that temperature for 2 hours and the second charge of co-resin was added and an epoxy equivalent was obtained. The second charge of methyl isobutyl ketone, crosslinker, methyl isobutyl ketone, and diethanolamine were added sequentially. The reaction mixture was allowed to exotherm and a temperature of 122°C was established. The reaction mixture was held at 122°C for 30 minutes and diketimine was added and the mixture held at 122°C for one hour. EPON 880 (85% solution in methyl isobutyl ketone) was added and the mixture was held for 30 minutes at 122°C. TINUVIN 123 then was added and the temperature was maintained at 122°C for 30 minutes. The reaction mixture (330 parts) was dispersed in aqueous medium by adding it to a mixture of 9.2 parts

of sulfamic acid and 225.7 parts of deionized water. To this was added 4.7 parts of surfactant (50/50 mixture of SURFYNOL 104 and the N-hydroxyethyl imidzoline of coconut fatty acid, neutralized to 75% total theoretical neutralization with acetic, 63.5% solids in ethylene glycol monobutyl ether) available from Air Products and Chemical, Inc. and 95 parts of a 30% solution of rosin acid in butylcarbitol formal. The dispersion was further diluted with 117.8 parts of deionized water and 127.1 parts of deionized water added in two stages. The dispersion was vacuum stripped to remove organic solvent yielding a dispersion having a solids content of 40.6 percent (one hour at 110°C).

#### EXAMPLE L

This example describes the preparation of a cationic acrylic resin having a blocked polyisocyanate curing agent mixed with the polymer. The cationic resin was used as a component in the electrodepositable coating composition of Example 7.

The acrylic resin was prepared as described below from the following ingredients:

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Methyl propyl ketone	274.78
TINUVIN® 1130	27.85
Ethyl acrylate	605.23
Styrene	463.25
Hydroxypropyl methacrylate	149.45
Methyl methacrylate	52.3
Glycidyl methacrylate	224.18
t-Dodecyl mercaptan	14.93
VAZO-67	37.34
PROPASOL B	47.83
DOWANOL PM	23.9
Methyl isobutyl ketone	19.38
LUPERSOL-75M	29.95
PROPASOL B	23.9
Methyl isobutyl ketone	4.78
Diethanolamine	134.16
Diketimine of Example I	109.68
Crosslinker <sup>1</sup>	1255.88
Sulfamic acid	88.51
Deionized water	7771.22

<sup>1</sup> Prepared by reacting one equivalent of isocyanurated hexamethylene diisocyanate with one mole of dibutylamine according to a procedure described in US 4,576,979.



The electrodepositable coating composition in the form of an electrodeposition bath was prepared by adding 800 parts of the deionized water to the cationic resin of Example K under agitation. The cationic resin of Example L was then added to the admixture. The pigment paste and catalyst paste were mixed separately under agitation and diluted with 500 parts of the deionized water, then blended into the reduced resin admixture under agitation. The remainder of the deionized water was then added under agitation. Final bath solids were about 22%, with a pigment to resin ratio of 0.15:1.0. The bath was allowed to agitate for two hours. Twenty percent of the total bath weight was removed by ultrafiltration and replaced with deionized water.

#### EXAMPLES 7A TO 7J

The following Examples 7A through 7I describe the preparation of electrodepositable coating compositions in the form of electrodeposition baths, each containing a rare earth element in accordance with the present invention. Comparative Example 7J describes the preparation of an electrodeposition bath comprising no rare earth element. The electrodepositable coating compositions were prepared as described below from the following ingredients.

#### EXAMPLE 7A

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Electrodepositable composition of Example 7	1600.0
Dysprosium nitrate <sup>1</sup>	2.0
Deionized water	97.1

<sup>1</sup>Commercially available from Alfa Aesar.

#### EXAMPLE 7B

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Electrodepositable composition of Example 7	1600.0
Erbium nitrate <sup>1</sup>	2.0
Deionized water	98.0

<sup>1</sup>Commercially available from Alfa Aesar.

EXAMPLE 7C

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Electrodepositable composition of Example 7	1600.0
Europium nitrate <sup>1</sup>	2.2
Deionized water	97.8

<sup>1</sup>Commercially available from Alfa Aesar.

5

EXAMPLE 7D

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Electrodepositable composition of Example 7	1600.0
Gadolinium acetate <sup>1</sup>	1.6
Deionized water	98.4

<sup>1</sup>Commercially available from Alfa Aesar.

EXAMPLE 7E

10

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Electrodepositable composition of Example 7	1600.0
Holmium nitrate <sup>1</sup>	2.0
Deionized water	98.0

<sup>1</sup>Commercially available from Alfa Aesar.

EXAMPLE 7F

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Electrodepositable composition of Example 7	1600.0
Lutetium nitrate <sup>1</sup>	1.6
Deionized water	98.6

<sup>1</sup>Commercially available from Alfa Aesar.

15

EXAMPLE 7G

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Electrodepositable composition of Example 7	1600.0
Neodymium acetate <sup>1</sup>	1.7
Deionized water	98.3

<sup>1</sup>Commercially available from Aldrich Chemical Company, Inc.

#### EXAMPLE 7H

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Electrodepositable composition of Example 7	1600.0
Praseodymium Nitrate <sup>1</sup>	2.2
Deionized water	97.8

<sup>1</sup>Commercially available from Acros Organics.

#### EXAMPLE 7I

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Electrodepositable composition of Example 7	1600.0
Samarium acetate <sup>1</sup>	1.6
Deionized water	98.4

<sup>1</sup>Commercially available from Aldrich Chemical Company, Inc.

#### COMPARATIVE EXAMPLE 7J

<u>INGREDIENTS</u>	<u>PARTS BY WEIGHT</u>
Electrodepositable composition of Example 7	1600.0
Deionized water	100.0

Each of the electrodepositable coating compositions of Examples 7A through 7I were prepared by first diluting the respective rare earth materials with the deionized water and then adding the mixture under agitation to the composition of Example 7. The composition of Comparative Example 7J was prepared by adding the deionized water to the electrodepositable composition of Example 7. Each composition was then allowed to agitate for least two hours.

#### ELECTROCOATING PROCEDURE:

Each of the electrodepositable coating compositions of Examples 7A to 7J above were electrodeposited onto phosphated cold rolled steel panels, commercially available from ACT Laboratories (phosphate treatment commercially available from PPG Industries, Inc., as Chemfos700, followed with a deionized water rinse.) Conditions for cationic electrodeposition were 2 minutes at 90°F at voltages required to yield a cured film thickness of 1.0 to 1.1 mils (25.4 micrometers). The coated substrates were cured in an electric oven at 360°F for 30 minutes.



### TESTING PROCEDURE:

Each of the coated steel test panels was single-scribed, cutting through the coating to the metal substrate, in an "I" pattern. The test panels were then subjected to cyclic corrosion testing in accordance with GM 9511P Standard.

- 5 Test panels were evaluated for "scribe creep" corrosion and visual appearance. Scribe creep is reported in millimeters of corrosion as a total scribe width. Test results are reported in the following TABLE 3.

TABLE 3

Example #	Rare earth metal	Scribe Creep* (mm)
7A	Dy	4
7B	Er	7
7C	Eu	4
7D	Gd	3.5
7E	Ho	3.5
7F	Lu	4.5
7G	Nd	6
7H	Pr	6
7I	Sm	6
7J**	---	9

\* Average scribe creep following 20 cycles GM 9511P.

\*\* Comparative example.

The data presented above in Table 3 illustrate that the inclusion of a rare earth metal in an electrodepositable coating composition of the present invention provides improved scribe creep corrosion resistance over an analogous composition which does not contain a rare earth metal.

### ALTERNATIVE EMBODIMENTS OF THE INVENTION:

#### EXAMPLE M

This example describes the preparation of a cationic resin in accordance with an alternative embodiment of the present invention. The cationic resin was prepared as described below.

Into a 3000 ml, 4-neck, round-bottom flask was charged 576.7 g (4.727 equivalents) of resorcinol diglycidyl ether having an EEW of 122 (available as Erisys RDGE from CVC Specialty Chemicals, Inc. of Maple Shade, NJ), 188.2 g (3.765 equivalents) of resorcinol, and 169.5 g of 1-butoxy-2-propanol. The flask was fitted with a stir paddle with bearing, a thermocouple probe, a heating mantle, a gas fitting, and a water-cooled condenser. Under a nitrogen blanket, the flask contents were heated to a temperature of 105°C and held at that temperature for 10 minutes, at which time 0.6 g of ethyltriphenylphosphonium iodide was added. The reaction mixture was allowed to exotherm, then the reaction mixture was adjusted to 160°C and that temperature was maintained for 105 minutes. The reaction mixture was then cooled to 100°C. At this time was added 58.3 g (0.155 mole) of an approximately 71% solution of the diketimine (formed from diethylenetriamine and excess methyl isobutyl ketone, such that the amine equivalent weight of the diketimine solution was 125), and 49.7 g (0.662 equivalents) of N-methylethanolamine. The reaction mixture was adjusted to 140°C and maintained at that temperature for at least 1.5 hours, then cooled to 80°C. Upon achieving that temperature, 745.9 g of crosslinker<sup>1</sup> and 11.0 g of SURFYNOL 104 (surfactant available from Air Products and Chemicals Inc.) were added, and the reaction mixture was mixed for 15 minutes. Of this mixture, 1500 g was added to a solution of 54.8 g (0.564 equivalents) of sulfamic acid in 781.2 g of deionized water. At least 20 minutes later, a total of 1335 g of additional deionized water was added. The resulting dispersion was diluted with an additional kilogram of deionized water, warmed to a temperature of 60° to 65°C, and solvent was co-distilled under reduced pressure to yield a dispersion which was found to be 46.6% non-volatile (one hour at 110°C).

<sup>1</sup> Crosslinker prepared as follows. Into a 5000 ml, 4-neck, round-bottom flask was charged 1136.2 g (8.788 equivalents) of dibutylamine and 86.4 g of methyl isobutyl ketone. The flask was then fitted with a stir paddle with bearing, a thermocouple probe, a gas fitting, a water-cooled condenser, a heating mantle, and an addition funnel. The addition funnel was charged with 1716.9 g (8.850 equivalents) of an hexamethylene diisocyanate trimer with an NCO equivalent weight of 194 (available as DESMODUR N-3300 from the Bayer Corporation) and 343.4 g of methyl isobutyl ketone and mixed to form a uniform solution. To the dibutylamine solution under a nitrogen blanket was added the isocyanurate solution, beginning at ambient temperature and the addition was continued at such a rate as to keep the reaction temperature below 80°C. At the completion of the addition, the funnel was rinsed with 73.8 g of methyl isobutyl ketone and the reaction was held at 80°C until an infrared spectrum of the reaction mixture revealed no more than a negligible NCO peak. At that point, the product was cooled. The resultant crosslinker had a solids content (one-hour at 110°C) of 85.1%.

### EXAMPLE N

This example describes the preparation of a cationic resin in accordance with an alternative embodiment of the present invention. The cationic resin was prepared as described below.

5 Into a 3000 ml, 4-neck, round-bottom flask was charged 617.9 g (5.327 equivalents) of resorcinol diglycidyl ether with an EEW of 116 (as used in Example M), 214.0 g (3.891 equivalents) of resorcinol, and 184.3 g of 1-butoxy-2-propanol. The flask was then equipped with a stir paddle with bearing, a thermocouple probe, a heating mantle, a gas fitting, and a water-cooled condenser.

10 Under a nitrogen blanket, this reaction mixture was heated to a temperature of 105°C. To the reaction mixture was added 0.7 g of ethyltriphenylphosphonium iodide, and the mixture was held at 105°C for 10 minutes. The temperature was then increased to 160°C, and the reaction mixture was maintained at that temperature for 105 minutes, at which time the reaction mixture was cooled to a temperature of

15 100°C and sampled to find that the epoxy equivalent weight ("EEW") was 875 based on solids. 63.4 g (0.169 mole) of the diketimine (as described in Example M above), and 54.1 g (0.720 equivalents) of N-methylethanolamine then were added to the reaction mixture, and the temperature was increased to 140°C. The temperature was maintained at 140°C for 80 minutes and the EEW was found to be 33,000 on

20 solids. This material was cooled to 80°C at which time 653.7 g of crosslinker<sup>1</sup> and 12.0 g of SURFYNOL104 were added and the reaction mixture was blended for 15 minutes. Of this product, 1500 g was poured into a solution of 59.6 g (0.614 equivalents) of sulfamic acid in 759.9 g of deionized water, and the mixture was blended for at least 20 minutes, at which time 1325 g of additional deionized water

25 was added. This dispersion was further diluted with a kilogram of deionized water and warmed to a temperature of 60° to 65°C, whereupon the solvent was co-distilled under reduced pressure to yield a dispersion having a solids content of 32.7% (one hour at 110°C).

<sup>1</sup> Crosslinker prepared as follows. Into a 5000 ml, 4-neck, round-bottom flask was charged

30 630.3 g (4.886 equivalents) of dibutylamine and 210.1 g of methyl isobutyl ketone. The flask was then fitted with a stir paddle with bearing, a thermocouple probe, a gas fitting, a water-cooled condenser, a heating mantle, and an addition funnel. The addition funnel was charged with 645.0 g (4.886 equivalents) of a methylene diphenyl diisocyanate ("MDI") having an NCO equivalent weight of 132 (available as PAPI ® 2940 from Dow Chemical Company). To the

35 stirred dibutylamine solution under a nitrogen blanket, beginning at ambient temperature, was added the MDI at such a rate as to keep the temperature under 70°C. When the addition was completed, the funnel was rinsed with 14.7 g of methyl isobutyl ketone and the reaction mixture was adjusted to 70°C. The temperature was maintained at 70°C until an infrared

spectrum of a sample of the reaction mixture indicated no more than a negligible NCO peak. The reaction mixture was cooled. The resultant crosslinker was found to have a solids content of 85.9% (one-hour at 110°C).

5

#### EXAMPLE O

This example describes the preparation of a cationic resin in accordance with an alternative embodiment of the present invention. The cationic resin was prepared as described below.

10 Into a 5000 ml, 4-neck, round-bottom flask was charged 955.6 g (4.550 equivalents) of a saturated epoxy having an EEW of 210 (available as EPONEX 1510 from Shell Oil and Chemical Company), 182.8 g (3.324 equivalents) of resorcinol, and 157.5 g of 1-butoxy-2-propanol. The flask was then fitted with a stir paddle with bearing, a thermocouple probe, a gas fitting, a water-cooled condenser, and a heating mantle. Under a nitrogen blanket, the mixture was heated to 105°C, at  
15 which time 0.6 g of ethyltriphenylphosphonium iodide was added, and heating was continued to attain a temperature of 160°C. The reaction mixture maintained at 160°C for a period of 105 minutes, then cooled to 100°C. The EEW was determined to be 1244 based on solids. At that point, 54.2 g (0.144 mole) of the ketimine (as described in Example M above) and 46.2 g (0.615 equivalents) of N-  
20 methylethanolamine were added, and the temperature was adjusted to 140°C. This temperature was maintained for 1.5 hours, whereupon the EEW was found to be infinite. The reaction mixture was cooled to 80°C and 693 g of crosslinker (as described in Example M above) and 10.2 g of SURFYNOL 104 were added and the reaction mixture was blended to homogeneity over a period of 15 minutes. Of this  
25 material, 1500 g was poured into a solution of 43.6 g (0.449 equivalents) of sulfamic acid in 872.1 g of deionized water. This mixture was blended under agitation for a period of 20 minutes at which time 1081 g of deionized water were added. This dispersion was then diluted with a kilogram of deionized water, warmed to a temperature of 60° to 65°C, and exposed to reduced pressure to co-distill the solvent,  
30 resulting in a dispersion having a solids content of 43.3% (one hour at 110°C).

#### EXAMPLE P

This example describes the preparation of a cationic epoxy resin for use in the alternative electrodepositions of the present invention. The cationic resin was  
35 prepared as described below.

Into a 3000 ml, 4-neck, round-bottom flask was charged 920.8 g (4.898 equivalents) of a bisphenol A diglycidyl ether resin having an epoxy equivalent of 188 (EPON 880, available from Shell Oil and Chemical Company), 196.7 g (3.576 equivalents) of resorcinol, and 169.5 g of 1-butoxy-2-propanol. The flask was then fitted with a paddle stirrer with bearing, a thermocouple probe, a gas fitting, a water-cooled condenser, and a heating mantle. Under a nitrogen blanket, the mixture was heated to a temperature of 105°C, 0.6 g of ethyltriphenylphosphonium iodide was added, and heating was continued to a temperature of 160°C. The temperature was held at 160°C for a period of 105 minutes, then cooled to 100°C at which time it was determined that the EEW based on solids was 1118. 58.3 g (0.155 mole) of the diketimine (as described in Example M above), and 49.7 g (0.662 equivalent) of N-methylethanolamine were added, and the reaction mixture was heated to 140°C and held at that temperature for six hours. The EEW based on solids was determined to be 9757 after two hours. The reaction mixture was then cooled to 80°C and 745.9 g of crosslinker (as described in Example M above), and 11.0 g of SURFYNOL 104 were added and mixed for 15 minutes. Of this material, 1500 g was poured into a solution of 45.8 g (0.472 equivalent) of sulfamic acid in 854.3 g of deionized water. The reaction mixture was mixed for 20 minutes and 1372 g of deionized water were added. The dispersion was further diluted with a kilogram of deionized water, heated to a temperature of 60°C to 65°C and subjected to co-distillation under reduced pressure to remove the organic solvent. The final, dispersion had a solids content of 37.8% (one hour at 110°C).

#### EXAMPLE Q

This example describes the preparation of a cationic epoxy resin used as a component in the electrodepositable coating compositions of the alternative embodiment of the present invention. The cationic resin was prepared as described below.

Into a 5000 ml, 4-neck, round-bottom flask was charged 656.7 g (3.127 equivalents) of a saturated epoxy with EEW of 210 (available as EPONEX 1510 from Shell Oil and Chemical Company), 108.2 g (1.967 equivalents) of resorcinol, and 169.5 g of 1-butoxy-2-propanol. The flask was then fitted with a stir paddle with bearing, a thermocouple probe, a gas fitting, a water-cooled condenser, and a heating mantle. Under a nitrogen blanket, the mixture was heated to 105°C, at which

time 0.6 g of ethyltriphenylphosphonium iodide was added, and heating was continued to attain a temperature of 160°C. The reaction mixture was maintained at 160°C for a period of 105 minutes, cooled to 100°C, and the EEW was determined to be 877 based on solids. 58.3 g (0.156 mole) of the diketimine (as described in Example M above) and 49.7 g (0.662 equivalent) of N-methylethanolamine were added, and the temperature was adjusted to 140°C. This temperature was maintained for 1.5 hours, whereupon the EEW was found to be infinite. The reaction mixture then was cooled to 80°C and 745.9 g of crosslinker (prepared as described in Example M above) and 11 g of SURFYNOL 104 were added and mixed to homogeneity over a period of 15 minutes. Of this material, 1500 g was poured into a solution of 54.8 g (0.564 equivalent) of sulfamic acid in 781.2 g of deionized water. The reaction mixture was blended for 20 minutes and a total of 1045 g of deionized water was added. This dispersion was then diluted with a kilogram of deionized water, warmed to a temperature of 60°C to 65°C, and co-distilled under reduced pressure to remove organic solvent. The final dispersion had a solids content of 48.0% (one hour at 110°C).

#### EXAMPLE R

This example describes the preparation of a cationic epoxy resin used as a component in the electrodepositable coating compositions of the alternative embodiment of the present invention. The cationic resin was prepared as described below.

Into a 3000 ml, 4-neck, round-bottom flask was charged 642.1 g (3.415 equivalents) of a bisphenol A diglycidyl ether resin having an epoxy equivalent of 188 (EPON 880, available from Shell Oil and Chemical Company), 122.7 g (2.231 equivalents) of resorcinol, and 169.5 g of 1-butoxy-2-propanol. The flask was then fitted with a paddle stirrer with bearing, a thermocouple probe, a gas fitting, a water-cooled condenser, and a heating mantle. Under a nitrogen blanket, the mixture was heated to 105°C, 0.6 g of ethyltriphenylphosphonium iodide was added, and heating was continued to reach a temperature of 160°C. The temperature was held at 160°C for a period of 105 minutes, then cooled to 100°C at which time it was determined that the EEW based on solids was 735. 58.3 g (0.155 mole) of diketimine (as described in Example M above) and 49.8 g (0.662 equivalent) of N-methylethanolamine were added, and the reaction mixture was heated to 140°C and

held at that temperature for six hours. The EEW based on solids was determined to be 9071 after 1.5 hours. The reaction mixture was then cooled to 80°C and 746.1 g of crosslinker (described in Example M above) and 11.0 g of SURFYNOL 104 were added and mixed for 15 minutes. Of this material, 1500 g was poured into a solution of 54.8 g (0.565 equivalent) of sulfamic acid in 781.2 g of deionized water. The reaction mixture was blended for 20 minutes at which time 1335 g of deionized water was added. The dispersion was further diluted with a kilogram of deionized water, heated to a temperature of 60°C to 65°C and co-distilled under reduced pressure to remove organic solvent. The final dispersion had a solids content of 42.0% (one hour at 110°C).

#### EXAMPLE S

This example describes the preparation of a cationic epoxy resin used in the electrodepositable coating compositions of the alternative embodiment of the present invention. The cationic resin was prepared as described below.

Into a 3000 ml, 4-neck, round-bottom flask was charged 568.2 g (4.898 equivalents) of resorcinol diglycidyl ether having an EEW of 116, 196.7 g (3.576 equivalents) of catechol, and 169.5 g of 1-butoxy-2-propanol. The flask was fitted with a stir paddle with bearing, a thermocouple probe, a heating mantle, a gas fitting, and a water-cooled condenser. Under a nitrogen blanket, the flask contents were heated to a temperature of 105°C and that temperature was maintained for 10 minutes at which time 0.6 g of ethyltriphenylphosphonium iodide was added. The reaction mixture was allowed to exotherm, then the reaction temperature was adjusted to 160°C and held for a period of 105 minutes. The reaction mixture was then cooled to 100°C at which time, the EEW based on solids was found to be 754. To this was added 58.3 g (0.155 mole) of diketimine (described in Example M above) and 49.7 g (0.662 equivalent) of N-methylethanolamine. The reaction temperature was adjusted to 140°C and held for one hour, whereupon the EEW based on solids was found to be 29,750. The reaction mixture was then cooled to 80°C. At that temperature, 745.9 g of crosslinker (prepared as described in Example M above) and 11.0 g of SURFYNOL 104 were added, and the reaction mixture was mixed for 15 minutes. Of this mixture, 1500 g was added to a solution of 54.8 g (0.564 equivalents) of sulfamic acid in 781.2 g of deionized water. The mixture was agitated for 20 minutes at which time 1335 g of deionized water was added. The resulting

dispersion was diluted with a kilogram of deionized water, warmed to a temperature of 60°C to 65°C, and solvent was co-distilled under reduced pressure to yield a dispersion having a solids content of 38.3% (one hour at 110°C).

5

#### EXAMPLE T

This example describes the preparation of a cationic epoxy resin used in the electrodepositable coating compositions of the alternative embodiment of the present invention. The cationic resin was prepared as described below.

10 Into a 3000 ml, 4-neck, round-bottom flask was charged 568.2 g (4.898 equivalents) of resorcinol diglycidyl ether having an EEW of 116, 196.7 g (3.576 equivalents) of hydroquinone, and 169.5 g of 1-butoxy-2-propanol. The flask was fitted with a stir paddle with bearing, a thermocouple probe, a heating mantle, a gas fitting, and a water-cooled condenser. Under a nitrogen blanket, the flask contents were heated to 105°C and held at that temperature for 10 minutes, at which time 0.6 g of ethyltriphenylphosphonium iodide was added. The reaction mixture was allowed to exotherm, then the reaction mixture was adjusted to 160°C and held at that temperature for a period of 105 minutes. The reaction mixture was then cooled to 100°C at which time the EEW based on solids was found to be 695. To the reaction mixture then was added 58.3 g (0.155 mole) of diketimine (prepared as described above in Example M) and 49.7 g (0.662 equivalent) of N-methylethanolamine. The reaction mixture temperature was adjusted to 140°C and that temperature maintained for at least 2.5 hours, then cooled to 80°C. At that temperature, 745.9 g of crosslinker (prepared as described in Example M above) and 11.0 g of SURFYNOL 104 were added, and the agitation was continued for 15 minutes. Of this mixture, 1500 g was added to a solution of 54.8 g (0.564 equivalent) of sulfamic acid in 781.2 g of deionized water. The reaction mixture was blended for 20 minutes and 1335 g of additional deionized water was added. The resulting dispersion was diluted with one kilogram of deionized water, warmed to a temperature of 60° to 65°C, and solvent was co-distilled under reduced pressure to yield a dispersion having a solids content of 39.9% (one hour at 110°C).

#### EXAMPLE 8 through 15

The following Examples 8 – 15 describe the preparation of electrodepositable coating compositions (in the form of electrodeposition baths) in accordance with the



alternative embodiment of the present invention. The electrodepositable coating compositions comprise the cationic resins of Examples M through T.

#### EXAMPLE 8

This example describes the preparation of an electrodepositable coating composition of the alternative embodiment of the present invention. The electrodeposition bath was prepared as described below from the following ingredients.

INGREDIENTS	Parts by Weight (grams)	Parts Solids by Weight (grams)
Cationic resin of Example M	1514.2	705.6
Pigment paste <sup>1</sup>	166.5	118.8
Catalyst paste <sup>2</sup>	22.0	11.7
Deionized water	2097.3	---

<sup>1</sup> A pigment paste was prepared from a mixture of the following ingredients by processing in a sand-mill to a Hegman value of 7.

INGREDIENTS	Parts by Weight	Parts Solids
Grind resin <sup>a</sup>	1612.9	500.0
Carbon black pigment <sup>b</sup>	30.0	30.0
Titanium dioxide pigment <sup>c</sup>	2970.0	2970.0
Deionized water	387.1	---

<sup>a</sup> Prepared as described in U.S. Patent No. 5,130,004, Example F, except that the ethylene glycol monobutyl ether was replaced with a mixture of propylene glycol butyl ether and propylene glycol methyl ether, having a solids content of 31.0%.

<sup>b</sup> CSX-333, available from Cabot Corp. as Raven 410.

<sup>c</sup> Available from Kerr-McGee Corp. as Tronox CR-800E.

<sup>2</sup> A catalyst paste was prepared from the following ingredients by forming an admixture and processing in a sand-milled to a Hegman value of 7.

INGREDIENTS	Parts by Weight	Parts Solids
Grind vehicle <sup>a</sup>	407.7	126.4
Dibutyltin oxide <sup>b</sup>	191.6	191.6
Deionized water	0.7	---

<sup>a</sup> Prepared as described in U.S. Patent No. 5,130,004, Example F, except that the ethylene glycol monobutyl ether was replaced with a mixture of propylene glycol butyl ether and propylene glycol methyl ether, having a solids content of 31.0%.

<sup>b</sup> Available from Atofina Chemicals as Fascat 4201.

The resulting electrodeposition bath solids was content for each of the baths was 22% and the pigment to binder ratio was 0.15: 1.0. Twenty percent by weight of each bath composition was removed by ultrafiltration, and replaced with deionized water.

### EXAMPLES 9 THROUGH 15

Electrodepositable coating compositions of Examples 9 through 15, in the form of electrodeposition baths, were prepared exactly as in Example 8 above except that the amounts of cationic resins of Example N through T, respectively, were adjusted to produce 705.6 parts of solids and the amounts of deionized water were accordingly adjusted to produce 3800 parts by weight of electrodeposition bath for each example.

### TESTING PROCEDURES:

Each of the electrodepositable coating compositions of the alternative embodiment of the present invention (Examples 8 – 15) were electrodeposited onto various test substrates under conditions sufficient to provide an electrodeposited film thickness of about 1 mil (25.4 micrometers). The various substrates, curing conditions, and test methods used to evaluate for corrosion resistance and photodegradation resistance are as described in the following Table 4. It should be noted that for Xenon Arc Weatherometer testing, the cured electrocoated test panels were subsequently coated with the unpigmented base coat/clear coat system (providing 80% light transmission at 400 nanometers) which was described above with reference to Examples 1-5.

TABLE 4

CORROSION RESISTANCE AND DURABILITY

Test		20 day Salt Spray <sup>1</sup> Scribe Creep (mm)		20 GM Cycle B, mm Total Scribe Creep <sup>2</sup>				Xenon Arc WeatherOMeter <sup>7</sup> (10 = best)	WeatherOMeter hours to failure (6 rating or less)	
Example #	Cure Conditions	Bare Steel Substrate <sup>3</sup>	Bare Steel Substrate <sup>3</sup>	Steel Substrate (Chemfos C700 Phosphate, Deionized Water Rinse) <sup>4</sup>	Electrogalvanized Steel (Chemfos C700 Phosphate, Deionized Water Rinse) <sup>5</sup>	Zinc-Iron Alloy (Chemfos C700 Phosphate, Deionized Water Rinse) <sup>6</sup>	Steel (Chemfos C700 Phosphate, Deionized Water Rinse) <sup>4</sup>			
8	60° @ 385°F	9.5	29	5	1	1	10		no failure @ 3759 hr.	
8	30° @ 350°F	8.5	12	5	1	1	10		no failure @ 3759 hr.	
8	30° @ 325°F	9	12	7	1	1	9.5		no failure @ 3759 hr.	
9	60° @ 385°F	4.5	10	2	2	1	0		1500 hr.	
9	30° @ 350°F	4.5	10	3	2	1	0		1000 hr.	
9	30° @ 325°F	6	7	3	2	1	0		1000 hr.	
10	60° @ 385°F	15	13	4	2	1	6		3759 hr.	
10	30° @ 350°F	12.5	7	5	1	1	8		no failure @ 3759 hr.	
10	30° @ 325°F	12	8	7	1	1	8.5		no failure @ 3759 hr.	
11	60° @ 385°F	2	9	4	1	1	0		2500 hr.	
11	30° @ 350°F	6	14	3	1	1	0		3200 hr.	
11	30° @ 325°F	4.5	Total delamination	4	1	1	0		3200 hr.	
12	60° @ 385°F	Total delamination	Total delamination	8	1	2	7.5		no failure @ 3759 hr.	
12	30° @ 350°F	17.5	Total delamination	5	2	2	8		no failure @ 3759 hr.	
12	30° @ 325°F	20	9	8	2	2	8.5		no failure @ 3759 hr.	
13	60° @ 385°F	11	Total delamination	6	2	3	9		no failure @ 3759 hr.	
13	30° @ 350°F	8	Total delamination	6	1	2	8		no failure @ 3759 hr.	
13	30° @ 325°F	11	17	5	1	2	8		no failure @ 3759 hr.	
14	60° @ 385°F	7.5	14	3	1	1	10		no failure @ 3759 hr.	
14	30° @ 350°F	5	12	4	1	1	10		no failure @ 3759 hr.	
14	30° @ 325°F	5.5	12	5	2	1	10		no failure @ 3759 hr.	
15	60° @ 385°F	11	12	4	1	1	9		no failure @ 3759 hr.	
15	30° @ 350°F	10	10	4	1	1	7		no failure @ 3759 hr.	
15	30° @ 325°F	11.5	7	5	1	1	9		no failure @ 3759 hr.	

5

<sup>1</sup> According to ASTM B117.  
<sup>2</sup> According to General Motors Engineering Standard 9540P, Method B.  
<sup>3</sup> Available from Advanced Coating Technologies, Inc. as APR28110.  
<sup>4</sup> Available from Advanced Coating Technologies, Inc. as APR28630.  
<sup>5</sup> Available from Advanced Coating Technologies, Inc. as APR31611.  
<sup>6</sup> Available from Advanced Coating Technologies, Inc. as APR32457.  
<sup>7</sup> Tested according to ASTM J1960, using an Atlas Model C165XWA WeatherOMeter using Type S borosilicate inner and outer filters  
<sup>8</sup> 3759 hr. exposure under clear basecoat/clearcoat with 80% transmission @ 400 nm, A 2mm, 6 teeth cross-cutting tool (Byk-Gardner Model PA-2056) was used according to ASTM D3359-97, except that a 1 to 10 rating system was employed

10

Example 8 versus 9 is a comparison of aliphatic versus aromatic isocyanate. The data in Table 4 illustrate that aliphatic isocyanate provides improved durability over aromatic isocyanate however, aliphatic isocyanates are poorer for corrosion resistance on steel substrates.

Examples 8 versus 10 versus 11 represent a comparison of resorcinol diglycidyl ether to saturated epoxy to aromatic bisphenol A epoxy extended with equal amounts of resorcinol. The data of Table 4 illustrate that resorcinol diglycidyl ether provides improved durability over the saturated epoxy analog which gives better durability than the composition comprising bisphenol A. Aromatic bisphenol A epoxy however, gave the best corrosion resistance over steel substrates.

Examples 8 versus 12 versus 13 represents a comparison of resorcinol diglycidyl ether to saturated epoxy to aromatic bisphenol A epoxy extended with resorcinol, using amounts permitting comparison at equal levels of crosslinker. The data in Table 4 illustrate that the resorcinol diglycidyl ether provides improved durability over either the saturated or the aromatic bisphenol A epoxy. Also resorcinol has the best overall corrosion resistance.

Examples 8 versus 14 versus 15 represents a comparison of resorcinol-to catechol- and hydroquinone- extended resorcinol diglycidyl ether. The data presented in Table 4 illustrate that each of these compositions gave good durability and corrosion resistance, with the catechol version being slightly improved in both categories.

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications which are within the spirit and scope of the invention, as defined by the appended claims.